Synthesis of Polycyclic Substituted Vinylarenes via a One-Pot Intramolecular Aryl Alkylation/*N*-Tosylhydrazone Insertion Reaction

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Supporting Information

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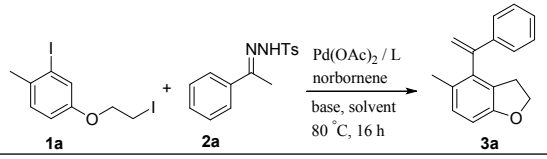
1. General Remarks

For product purification by flash column chromatography, silica gel (200~300 mesh) and light petroleum ether (bp. 60~90) are used. ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$ using TMS as internal standard. IR spectra were recorded on a FT-IR spectrometer and only major peaks were reported in cm^{-1}. Melting points were determined on a microscopic apparatus and were uncorrected. All products were further characterized by HRMS (high resolution mass spectra). Copies of their ^{1}H NMR and ^{13}C NMR spectra were provided. dioxane were dried over Na. Commercially available reagents and solvents were used without further purification.

2. Optimization of the reaction conditions

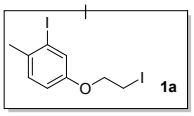


Entry	Base	Solvent	Ligand	Yield, %[b]
1	K_2CO_3	DME	PPh_3	67
2	K_2CO_3	dioxane	PPh_3	71
3	K_2CO_3	THF	PPh_3	60
4	K_2CO_3	CH_3CN	PPh_3	53
5	*t*-BuOLi	dioxane	PPh_3	0
6	Cs_2CO_3	DME	PPh_3	70
7	Cs_2CO_3	dioxane	PPh_3	74
8	Cs_2CO_3	dioxane	Xphos	23
9	Cs_2CO_3	dioxane	TFP	55
10	Cs_2CO_3	dioxane	dppe	0
11	Cs_2CO_3	dioxane	dppb	0
12	Cs_2CO_3	dioxane	-	0
13[c]	Cs_2CO_3	dioxane	PPh_3	89
14[c]	K_2CO_3	dioxane	PPh_3	80
15[d]	Cs_2CO_3	dioxane	PPh_3	84
16[e]	Cs_2CO_3	dioxane	PPh_3	61
17[f]	Cs_2CO_3	dioxane	PPh_3	0

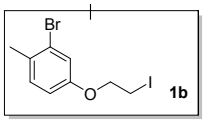
[a]Reaction conditions : **1a** (0.2 mmol), **2a** (0.4 mmol), $Pd(OAc)_2$ (10 % mmol), ligand (20 % mmol), base (5.0 equiv.), norbornene (1.0 equiv.), solvent (2 ml), 80 °C, 16 h. [b]Yield of the isolated product. [c]The reaction was carried out with 5.0 equivalents of H_2O. [d]The reaction was carried out with 0.5 equivalents of norbornene and 5.0 equivalents of H_2O. [e]The reaction was carried out with 0.25 equivalents of norbornene and 5.0 equivalents of H_2O. [f]The reaction was carried out 5.0 equivalents of H_2O and without norbornene.

3. Preparation of Starting Materials

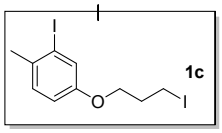
N-tosylhydrazones **2a-2s** were prepared according to a previously reported literature[1]. **1a-1i, 4a-4d, 4t** were prepared by literature procedure [2].



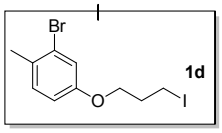
2-iodo-4-(2-iodoethoxy)-1-methylbenzene (1a): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36 (d, *J* = 2.8 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.81 (dd, *J* = 2.8 Hz, *J* = 8.4 Hz, 1H), 4.19 (t, *J* = 6.8 Hz, 2H), 3.39 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.1, 134.2, 129.8, 125.0, 114.9, 100.8, 68.9, 26.9, 1.2.



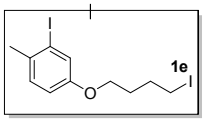
2-bromo-4-(2-iodoethoxy)-1-methylbenzene (1b): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.13-7.09 (m, 2H), 6.79-6.75 (m, 1H), 4.25-4.17 (m, 2H), 3.61 (t, *J* = 6.4 Hz, 1H), 3.38 (t, *J* = 6.4 Hz, 1H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.5, 131.1, 130.5, 124.9, 118.6, 114.0, 68.9, 21.9, 0.9.



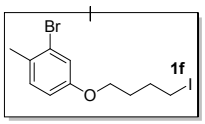
2-iodo-4-(3-iodopropoxy)-1-methylbenzene (1c): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.37 (d, *J* = 2.4 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.81 (dd, *J* = 2.4 Hz, *J* = 8.4 Hz, 1H), 3.99 (t, *J* = 6.4 Hz, 2H), 3.35 (t, *J* = 6.8 Hz, 2H), 2.36 (s, 3H). 2.28-2.22 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.2, 133.6, 1297, 124.7, 114.7, 100.8, 67.5, 32.8 26.9, 2.4.



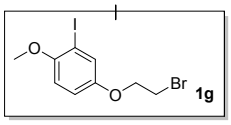
2-bromo-4-(3-iodopropoxy)-1-methylbenzene (1d): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.11-7.09 (m, 2H), 6.76-6.73 (m, 1H), 3.96 (t, *J* = 6.0 Hz, 2H), 3.33 (t, *J* = 6.0 Hz, 1H), 2.31 (s, 3H), 2.25-2.19 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.1, 130.9, 129.9, 124.8, 118.2, 113.7, 67.5, 32.7, 21.8, 2.4.



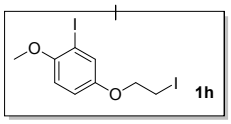
2-iodo-4-(4-iodobutoxy)-1-methylbenzene (1e): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.33 (d, *J* = 2.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.77 (dd, *J* = 2.4 Hz, *J* = 8.4 Hz, 1H), 3.93-3.89 (m, 2H), 3.25-3.21 (m, 2H), 2.35 (s, 3H), 2.02-1.95 (m, 2H), 1.90-1.82 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 156.9, 133.2, 129.6, 124.4, 114.5, 100.8, 66.8, 33.4, 30.0, 26.8, 6.4.



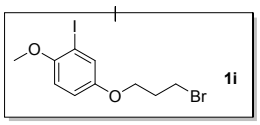
2-bromo-4-(4-iodobutoxy)-1-methylbenzene (1f): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.12-7.07 (m, 2H), 6.75-6.73 (m, 1H), 3.95-3.91 (m, 2H), 3.25 (t, *J* = 6.0 Hz, 2H), 2.31 (s, 3H), 2.06-1.84 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.4, 131.0, 129.7, 124.8, 118.1, 113.8, 66.9, 30.1, 30.0, 21.8, 6.3.



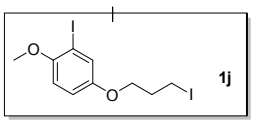
4-(2-bromoethoxy)-2-iodo-1-methoxybenzene (1g): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36 (d, *J* = 3.2 Hz, 1H), 6.80 (dd, *J* = 3.2 Hz, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 8.8 Hz,1H), 4.21 (t, *J* = 6.4 Hz, 2H), 3.82 (s, 3H), 3.60 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.1, 152.4, 126.0, 115.7, 111.2, 85.9, 68.7, 56.8, 29.1.



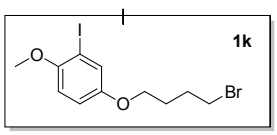
2-iodo-4-(2-iodoethoxy)-1-methoxybenzene (1h): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.36-7.35 (m, 1H), 6.90-6.87 (m, 1H), 6.76-6.73 (m, 1H), 4.23-4.15 (m, 2H), 3.83 (s, 3H), 3.60 (d, *J* = 6.0 Hz, 1H), 3.38 (d, *J* = 6.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.1, 152.3, 126.1, 115.8, 111.3, 85.9, 69.5, 56.8, 1.2.



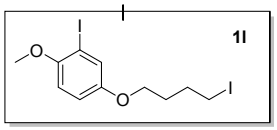
4-(3-bromopropoxy)-2-iodo-1-methoxybenzene (1i): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35 (d, *J* = 2.8 Hz, 1H), 6.87 (dd, *J* = 9.2 Hz, *J* = 2.8 Hz, 1H), 6.75 (d, *J* = 9.2 Hz,1H), 4.03 (t, *J* = 5.6 Hz, 2H), 3.83 (s, 3H), 3.60 (d, *J* = 6.4 Hz, 2H), 2.31-2.25 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2, 152.8, 125.6, 115.3, 111.4, 85.9, 66.0, 56.9, 32.2, 30.0.



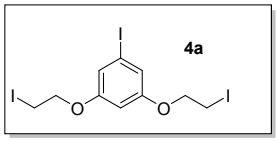
2-iodo-4-(3-iodopropoxy)-1-methoxybenzene (1j): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.35 (d, *J* = 3.2 Hz, 1H), 6.87 (dd, *J* = 3.2 Hz, *J* = 8.8 Hz, 1H), 6.75 (d, *J* = 8.8 Hz,1H), 3.96 (t, *J* = 5.6 Hz, 2H), 3.83 (s, 3H), 3.35 (d, *J* = 5.6 Hz, 2H), 2.26-2.20 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.2, 152.8, 125.6, 115.3, 111.4, 86.0, 68.0, 56.9, 32.8, 2.6.



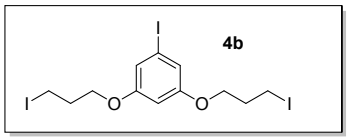
4-(4-bromobutoxy)-2-iodo-1-methoxybenzene (1k): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.33 (d, *J* = 2.8 Hz, 1H), 6.84 (dd, *J* = 2.8 Hz, *J* = 8.8 Hz, 1H), 6.73 (d, *J* = 8.8 Hz,1H), 3.91 (t, *J* = 6.0 Hz, 2H), 3.81 (s, 3H), 3.47 (d, *J* = 6.0 Hz, 2H), 2.07-2.00 (m, 2H), 1.93-1.86 (2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.3, 152.5, 125.4, 115.1, 111.4, 85.9, 67.5, 56.8, 33.4, 29.3, 27.7.



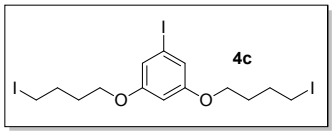
2-iodo-4-(4-iodobutoxy)-1-methoxybenzene (1l): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.33 (d, *J* = 2.8 Hz, 1H), 6.87-6.83 (m, 1H), 6.74 (d, *J* = 8.8 Hz,1H), 3.93-3.89 (m, 2H), 3.82 (s, 3H), 3.26 (d, *J* = 6.8 Hz, 2H), 2.05-1.97 (m, 2H), 1.90-1.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.4, 152.7, 125.4, 115.3, 111.4, 86.0, 67.4, 56.9, 30.1, 30.0, 6.5.



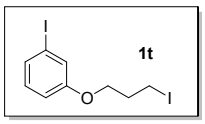
1-iodo-3,5-bis(2-iodoethoxy)benzene (4a): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 6.88 (dd, *J* = 2.4 Hz, *J* = 6.0 Hz,2H), 6.43 (dd, *J* = 2.4 Hz, *J* = 4.4 Hz,1H), 4.25-4.17 (m, 4H), 3.62 (t, *J* = 6.0 Hz, 2H), 3.39 (t, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.5, 117.1, 102.0, 94.1, 68.0, 0.6



1-iodo-3,5-bis(3-iodopropoxy)benzene (4b): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 6.86 (d, *J* = 2.0 Hz, 2H), 6.41 (dd, *J* = 2.4 Hz, *J* = 2.0 Hz,1H), 3.98 (t, *J* = 6.0 Hz, 4H), 3.34 (t, *J* = 6.0 Hz, 4H), 4.24 (dd, *J* = 6.0 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.0, 116.4, 101.4, 94.1, 67.4, 32.6, 2.4.



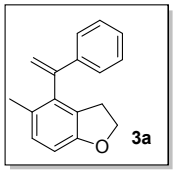
1-iodo-3,5-bis(4-iodobutoxy)benzene (4c): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 6.83 (d, *J* = 2.0 Hz, 2H), 6.37 (t, *J* = 5 Hz,1H), 3.92 (t, *J* = 6.0 Hz, 4H), 3.24 (t, *J* = 6.8 Hz, 4H), 2.05-1.96 (m, 4H), 1.90-1.83 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.2, 116.2, 101.3, 94.1, 66.8, 29.9, 29.8, 6.4.



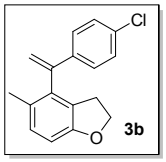
1-iodo-3-(3-iodopropoxy)benzene (1t): ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.29-7.25 (m, 2H), 7.00 (t, *J* = 8.0 Hz, 1H), 6.88-6.85 (m, 1H), 3.99 (t, *J* = 6.0 Hz, 2H), 3.35 (t, *J* = 6.8 Hz, 2H), 2.25 (dd, *J* = 6.0 Hz, *J* = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.1, 130.8, 130.0, 123.5, 114.1, 94.4, 67.3, 32.7, 2.4.

4. General procedure for the preparation of the products 3

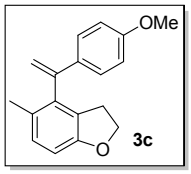
1 (0.2 mmol), **2** (0.4 mmol), $Pd(OAc)_2$ (4.5 mg,10 mol %), PPh_3 (10.5 mg, 20 mol %), norbornene (18.8 mg, 0.2 mmol, 1 equiv), Cs_2CO_3 (326 mg, 1 mmol, 5 equiv), H_2O (5equiv) were dissolved in 2 mL of degassed dry dioxane. The mixture was flushed with N_2 and stirred at room temperature for 15 minutes, then heated at 80 °C for 16 h. After cooling at room temperature, the mixture was diluted with diethyl ether, washed with water, dried over magnesium sufate, and purified by flash chromatography (silica, petroleum ether/AcOEt).



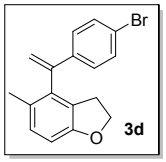
5-methyl-4-(1-phenylvinyl)-2,3-dihydrobenzofuran (3a): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.32-7.26 (m, 5H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.88 (d, *J* = 1.2 Hz, 1H), 5.17 (d, *J* = 1.2 Hz, 1H), 4.48 (t, *J* = 8.8 Hz, 2H), 2.94 (t, *J* = 8.8 Hz, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.8, 146.4, 139.2, 138.4, 133.8, 133.6, 129.2, 128.4, 127.8, 127.7, 126.3, 126.0, 114.5, 107.9, 71.2, 29.4, 18.9. IR (neat) 397, 2951, 2923, 2869, 1594, 1493, 1456, 1233, 986, 807, 706. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{17}H_{17}O$: 237.1274; Found, 237.1274.



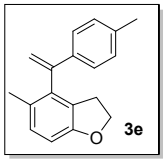
4-(1-(4-chlorophenyl)vinyl)-5-methyl-2,3-dihydrobenzofuran (3b): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.26-7.19 (m, 4H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.87 (s, 1H), 5.18 (s, 1H), 4.49 (t, *J* = 8.8 Hz, 2H), 2.93 (t, *J* = 8.8 Hz, 2H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.9, 145.3, 137.8, 137.7, 133.5, 129.4, 128.6, 127.7, 127.3, 126.2, 115.0, 108.1, 71.2, 29.4, 18.9. IR (neat) 3374, 2954, 2923, 1592, 1490, 1233, 1095, 908, 838, 734. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{17}H_{16}ClO$: 271.0884; Found, 271.0883.



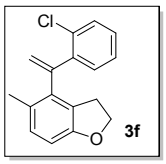
4-(1-(4-methoxyphenyl)vinyl)-5-methyl-2,3-dihydrobezofuran (3c): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.21 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.78 (d, *J* = 1.2Hz, 1H), 5.05 (d, *J* = 1.2Hz, 1H), 4.49 (t, *J* = 8.8 Hz, 2H), 3.80 (s, 3H), 2.95 (t, *J* = 8.8 Hz, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3, 157.8, 145.7, 138.7, 131.8, 129.2, 127.8, 127.2, 126.3, 113.8, 112.4, 107.8, 71.2, 55.2, 29.4, 18.9. IR (neat) 3396, 2924, 1604, 1510, 1458, 1295, 1248, 1034, 986, 837, 808. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{19}O_2$: 267.1380; Found, 267.1382.



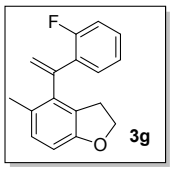
4-(1-(4-bromophenyl)vinyl)-5-methyl-2,3-dihydrobenzofuran (3d): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.40 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.88 (d, *J* = 0.8 Hz, 1H), 5.19 (d, *J* = 0.8 Hz, 1H), 4.50 (t, *J* = 8.8 Hz, 2H), 2.93 (t, *J* = 8.8 Hz, 2H), 2.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.9, 145.4, 138.2, 137.7, 131.6, 129.4, 127.8, 127.6, 126.3, 121.8, 115.1, 108.1, 71.2, 29.4, 18.9. IR (neat) 3370, 2953, 2924, 1737, 1592, 1508, 1456, 1388, 1232, 1009, 835, 734. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{17}H_{16}BrO$: 315.0379; Found, 315.0381.



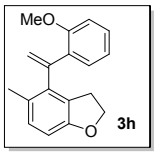
5-methyl-4-(1-(p-tolyl)vinyl)-2,3-dihydrobenzofuran (3e): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.17 (d, *J* = 8.0 Hz, 2H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.84 (d, *J* = 1.2Hz, 1H), 5.11 (d, *J* = 1.2Hz, 1H), 4.8 (t, *J* = 8.8 Hz, 2H), 2.94 (t, *J* = 8.8 Hz, 2H), 2.33 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7, 146.2, 138.6, 137.6, 136.3, 129.2, 129.1, 127.8, 126.3, 125.9, 113.5, 107.8, 71.2, 29.4, 21.1, 18.9. IR (neat) 3386, 2952, 1593, 1511, 1457, 1439, 1232, 986, 908, 827, 807, 734. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{19}O$: 251.1430; Found, 251.1426.



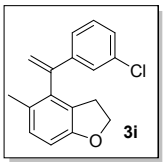
4-(1-(2-chlorophenyl)vinyl)-5-methyl-2,3-dihydrobenzofuran (3f): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.38-7.35 (m, 1H), 7.20-7.18 (m, 3H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 5.80 (d, *J* = 1.2 Hz, 1H), 5.50 (d, *J* = 1.2 Hz, 1H), 4.47 (t, *J* = 8.8 Hz, 2H), 2.94 (t, *J* = 8.8 Hz, 2H), 2.13 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.9, 144.3, 139.8, 138.4, 132.4, 130.9, 130.3, 129.7, 128.4, 127.7, 126.6, 126.2, 121.8, 108.1, 71.2, 29.9, 19.6. IR (neat) 3391, 2924, 2370, 1590, 1470, 1457, 1259, 1236, 1044, 909, 734. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{17}H_{16}ClO$: 271.0884; Found, 271.0883.



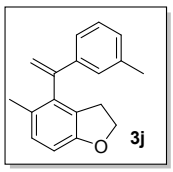
4-(1-(2-fluorophenyl)vinyl)-5-methyl-2,3-dihydrobenzofuran (3g): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.24-7.18 (m, 1H), 7.08-7.00 (m, 3H), 6.95 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 5.96 (s, 1H), 5.42 (s, 1H), 4.49 (t, *J* = 8.8 Hz, 2H), 2.97 (t, *J* = 8.8 Hz, 2H), 2.09 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.7, 159.3, 157.8, 141.2, 138.6, 130.1, 130.0, 129.3, 129.0, 127.6, 127.5, 126.1, 124.0, 123.9, 120.2, 120.1, 116.2, 116.0, 108.0, 71.2, 29.4, 19.0. IR (neat) 3395, 2951, 2924, 1606, 1593, 1487, 1455, 1218, 986, 920, 807, 755. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{17}H_{16}FO$: 255.1180; Found, 255.1176.



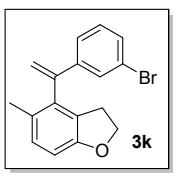
4-(1-(2-methoxyphenyl)vinyl)-5-methyl-2,3-dihydrobenzofuran (3h): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.24-7.20 (m, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 6.93-6.84 (m, 3H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.91 (d, *J* = 2.0 Hz, 1H), 5.32 (d, *J* = 2.0 Hz, 1H), 4.47 (t, *J* = 8.4 Hz, 2H), 3.71 (s, 3H), 2.96 (t, *J* = 8.4 Hz, 2H), 2.10 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.6, 157.5, 144.0, 139.9, 130.2, 129.5, 129.1, 128.6, 127.6, 126.0, 120.5, 119.2, 111.5, 107.4, 71.2, 55.5, 29.6, 19.1. IR (neat) 3384, 2951, 2870, 1595, 1490, 1457, 1243, 1027, 908, 753. HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{18}H_{19}O_2$: 267.1380; Found, 267.1385.



4-(1-(3-chlorophenyl)vinyl)-5-methyl-2,3-dihydrobenzofuran (3i): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.28-7.22 (m, 3H), 7.14-7.11 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.89 (s, 1H), 5.22 (s, 1H), 4.51 (t, *J* = 8.8 Hz, 2H), 2.94 (t, *J* = 8.8 Hz, 2H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.9, 145.4, 141.2, 137.6, 134.5, 129.7, 129.4, 127.8, 127.7, 126.3, 126.0, 124.3, 115.9, 108.2, 71.2, 29.4, 19.0. IR (neat) 3383, 2923, 2853, 1738, 1592, 1457, 1233, 1078, 907, 792. HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{17}H_{16}ClO$: 271.0884; Found, 271.0885.

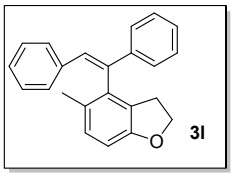


5-methyl-4-(1-(m-tolyl)vinyl)-2,3-dihydrobenzofuran (3j): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.19-7.15 (m, 1H), 7.11-7.04 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 5.86 (d, *J* = 1.2 Hz, 1H), 5.14 (d, *J* = 1.2 Hz, 1H), 4.49 (t, *J* = 8.8 Hz, 2H), 3.71 (s, 3H), 2.95 (t, *J* = 8.8 Hz, 2H), 2.31 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7, 146.5, 139.2, 138.5, 138.0, 129.2, 128.5, 128.3, 127.9, 126.5, 126.3, 123.3, 114.4, 107.8, 71.2, 29.4, 21.5, 19.0. IR (neat) 3383, 2953, 2922, 1596, 1456, 1440, 1299, 1234, 986, 906, 796. HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{17}H_{19}O$: 251.1430; Found, 251.1430.

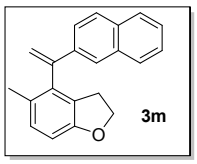


4-(1-(3-bromophenyl)vinyl)-5-methyl-2,3-dihydrobenzofuran (3k): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.46 (s, 1H), 7.39 (s, 1H), 7.16 (s, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.89 (s, 1H), 5.22 (s, 1H), 4.51 (t, *J* = 8.8 Hz, 2H), 2.94 (t, *J* = 8.8 Hz, 2H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.9, 145.2, 141.5, 137.5, 130.7, 130.0, 129.4, 128.9, 127.7, 126.3, 124.8, 122.8, 115.9, 108.2, 71.2, 29.4, 19.0. IR (neat) 3385, 2953, 2923,

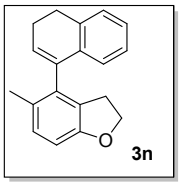
1590, 1558, 1456, 1295, 1233, 986, 907, 733, 671. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{17}H_{16}BrO$: 315.0379; Found, 315.0382.



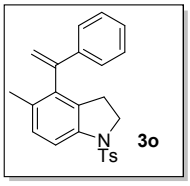
4-(1,2-diphenylvinyl)-5-methyl-2,3-dihydrobenzofuran (3l): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.34-7.26 (m, 5H), 7.18-7.12 (m, 3H), 7.08 (s, 1H), 7.02-6.99 (m, 3H), 6.73 (d, *J* = 8.0 Hz, 1H), 4.44-4.34 (m, 2H), 2.80-2.64 (m, 2H), 1.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.3, 141.0, 138.9, 137.1, 136.5, 129.8, 128.5, 128.4, 128.3, 128.2, 128.1, 127.5, 127.2, 126.3, 126.1, 108.2, 71.2, 29.2, 18.8. IR (neat) 3386, 2955, 2922, 2855, 1595, 1492, 1455, 1233, 981, 767, 695. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{23}H_{21}O$: 313.1587; Found, 313.1589.



5-methyl-4-(1-(naphthalen-2-yl)vinyl)-2,3-dihydrobenzofuran (3m): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.30 (d, *J* = 2.0 Hz, 1H), 7.88 (d, *J* = 2.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.50-7.43 (m, 2H), 7.41-7.35 (m, 1H), 7.25-7.22 (t, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.66 (d, *J* = 8.0 Hz, 1H), 5.79 (d, *J* = 1.2 Hz, 1H), 5.64 (d, *J* = 1.2 Hz, 1H), 4.42 (t, *J* = 8.8 Hz, 1H), 2.87 (t, *J* = 8.8 Hz, 1H), 2.18 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.0, 145.1, 139.2, 134.0, 131.0, 129.9, 128.6, 127.8, 127.6, 126.2, 126.0, 125.6, 125.5, 125.1, 121.3, 108.0, 71.2, 30.0, 19.8. IR (neat) 3049, 2952, 1847, 1590, 1458, 1264, 1232, 1057, 807, 781, 738. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{21}H_{19}O$: 287.1430; Found, 287.1430.

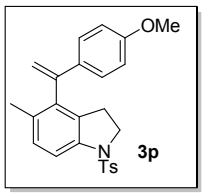


4-(3,4-dihydronaphthalen-1-yl)-5-methyl-2,3-dihydrobenzofuran (3n): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.20-7.11 (m, 2H), 7.06-7.02 (m, 1H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.92 (m, 1H), 4.54-4.44 (m, 2H), 3.11-3.03 (m, 1H), 2.91-2.79 (m, 3H), 2.46-2.41 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.7, 137.0, 136.9, 136.0, 134.2, 129.0, 128.4, 127.5, 127.4, 127.0, 126.7, 126.5, 124.2, 107.7, 71.2, 29.3, 28.1, 23.2, 18.8. IR (neat) 3382, 3018, 2933, 2830, 1594, 1457, 1236, 984, 909, 734. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{19}H_{19}O$: 263.1430; Found, 263.1429.

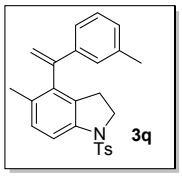


5-methyl-4-(1-phenylvinyl)-1-tosylindoline (3o): solid; m.p. 64-66 °C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.64 (d, *J*

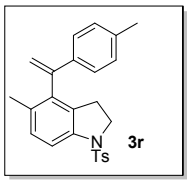
= 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.26-7.22 (m, 5H), 7.11-7.07 (m, 3H), 5.83 (d, *J* = 0.8 Hz, 1H), 5.02 (d, *J* = 0.8 Hz, 1H), 3.84 (t, *J* = 8.0 Hz, 2H), 2.53 (s, 2H), 2.39 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 143.8, 139.7, 138.7, 138.4, 134.2, 132.0, 131.6, 129.5, 129.3, 128.4, 127.8, 127.3, 125.8, 114.6, 114.5, 50.2, 27.4, 21.6, 19.1. IR(neat) 3378, 2955, 2869, 1618, 1579, 1452, 1353, 1167, 909, 814. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{24}H_{24}O_2NS$: 390.1522; Found, 390.1521.



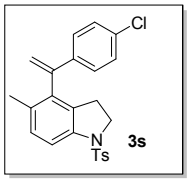
4-(1-(4-methoxyphenyl)vinyl)-5-methyl-1-tosylindoline (3p): solid; m.p. 87-89 °C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.64 (d, *J* = 8.4 Hz, 2H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.26-7.23 (m, 2H), 7.09-7.02 (m, 3H), 6.77-6.73 (m, 2H), 5.72 (d, *J* = 0.8 Hz, 1H), 4.90 (d, *J* = 0.8 Hz, 1H), 3.84 (t, *J* = 8.4 Hz, 2H), 3.78 (s, 3H), 2.53(d, *J* = 11.2 Hz, 2H), 2.40 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3, 145.0, 143.8, 139.7, 138.7, 134.2, 132.0, 131.5, 129.5, 129.3, 127.4, 127.0, 114.4, 113.7, 112.5, 55.2, 50.2, 27.4, 21.6, 19.0. IR (neat) 3385, 2956, 2853, 2055, 1602, 1510, 1455, 1352, 1249, 1164, 1031, 906, 815, 618. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{25}H_{26}O_3NS$: 420.1628; Found, 420.1626.



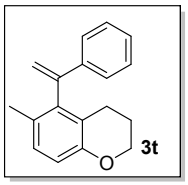
5-methyl-4-(1-(m-tolyl)vinyl)-1-tosylindoline (3q): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.65 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.25-7.22 (m, 2H), 7.10-7.04 (m, 3H), 6.98 (s, 1H), 6.84 (d, *J* = 8.0 Hz, 1H), 5.82 (s, 1H), 5.00 (s, 1H), 3.84 (t, *J* = 8.0 Hz, 2H), 2.54 (s, 2H), 2.38 (s, 3H), 2.27 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.7, 143.8, 139.7, 138.7, 138.6, 138.0, 134.2, 132.0, 131.4, 129.5, 129.3, 128.6, 128.3, 127.3, 126.3, 123.0, 114.5, 114.3, 50.1, 27.4, 21.5, 21.4, 19.1. IR (neat) 3384, 1598, 1454, 1354, 1167, 1092, 674. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{25}H_{26}O_2NS$: 426.1498; Found, 426.1496.



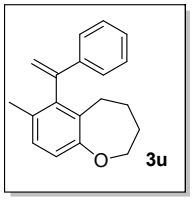
5-methyl-4-(1-(p-tolyl)vinyl)-1-tosylindoline (3r): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.64 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.26-7.22 (m, 2H), 7.09-6.98 (m, 5H), 5.79 (s, 1H), 4.96 (s, 1H), 3.84 (t, *J* = 8.0 Hz, 2H), 2.51 (m, 2H), 2.39 (s, 3H), 2.31 (s, 3H), 2.07 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 145.4, 143.8, 139.7, 138.6, 137.7, 135.8, 134.2, 132.0, 131.6, 129.5, 129.4, 129.3, 129.1, 127.3, 125.7, 114.5, 113.6, 50.2, 27.4, 21.6, 21.1, 19.1. IR (neat) 3381, 2953, 2923, 1598, 1511, 1454, 1354, 1166, 1093, 907, 815, 671. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{25}H_{26}O_2NS$: 404.1679; Found, 404.1677.



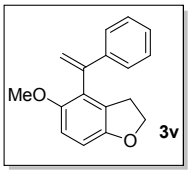
4-(1-(4-chlorophenyl)vinyl)-5-methyl-1-tosylindoline (3s): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.64 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.26-7.23 (m, 2H), 7.20-7.18 (m, 2H), 7.08 (d, *J* = 8.0 Hz, 1H), 7.02 (d, *J* = 8.0 Hz, 2H), 5.83 (s, 1H), 5.05 (s, 1H), 3.85 (t, *J* = 8.0 Hz, 2H), 2.50 (m, 2H), 2.40 (s, 3H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.5, 143.9, 139.9, 138.6, 137.9, 137.2, 134.2, 133.7, 131.9, 131.5, 129.6, 129.4, 128.6, 127.3, 127.1, 115.1, 114.7, 50.1, 27.4, 21.6, 19.0. IR (neat) 3383, 2922, 1597, 1491, 1354, 1166, 1092, 815, 587. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{24}H_{23}ClO_2NS$: 446.0952; Found, 446.0958.



6-methyl-5-(1-phenylvinyl)chroman (3t): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.29-7.25 (m, 5H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.73 (d, *J* = 8.0 Hz, 1H), 5.98 (s, 1H), 5.11 (s, 1H), 4.10 (t, *J* = 5.6 Hz, 2H), 2.77-2.69 (m, 1H), 2.33-2.26 (m, 2H), 2.09-2.07 (m, 4H), 1.92-1.83 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.9, 146.2, 141.4, 139.0, 128.5, 128.3, 127.7, 127.6, 125.7, 120.5, 115.5, 114.5, 65.9, 23.2, 22.5, 19.3. IR (neat) 3379, 2949, 2869, 1593, 1492, 1467, 1379, 1250, 1069, 813, 707. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{18}H_{19}O$: 251.1431; Found, 251.1430.

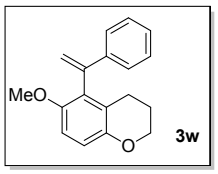


7-methyl-6-(1-phenylvinyl)-2,3,4,5-tetrahydrobenzo[b]oxepine (3u): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.28-7.24 (m, 5H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.96 (d, *J* = 0.8 Hz, 1H), 5.07 (d, *J* = 0.8 Hz, 1H), 4.09-3.90 (m, 2H), 2.78-2.66 (m, 2H), 2.08 (s, 3H), 1.92-1.86 (m, 2H), 1.51-1.44 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.9, 146.8, 141.2, 139.5, 134.5, 131.4, 128.4, 128.3, 128.1, 127.7, 125.9, 119.9, 114.4, 73.8, 32.4, 29.8, 25.9, 20,0. IR (neat) 3394, 2925, 2867, 1585, 1493, 1474, 1445, 1238, 1037, 906, 704. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{19}H_{21}O$: 265.1587; Found, 265.1588.

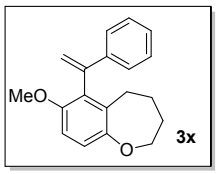


5-methoxy-4-(1-phenylvinyl)-2,3-dihydrobenzofuran (3v): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.33-7.24 (m, 5H), 6.71 (s, 1H), 5.88 (d, *J* = 1.2 Hz, 1H), 5.26 (d, *J* = 1.2Hz, 1H), 4.49 (t, *J* = 8.8 Hz, 2H), 3.62 (s, 3H), 2.96 (t, *J* = 8.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.8, 151.5, 143.9, 139.7, 128.4, 128.2, 127.9, 127.5, 126.0, 115.4, 111.1, 107.7, 71.7, 56.9, 29.6. IR (neat) 3400, 2926, 1603, 1458, 1326, 1227, 1072, 988, 781. HRMS-ESI (m/z) [M

+ H]$^+$ calcd for $C_{17}H_{17}O_2$: 253.1223; Found, 253.1222.



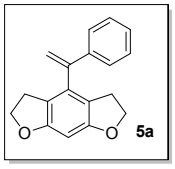
6-methoxy-5-(1-phenylvinyl)chroman (3w): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.32-7.23 (m, 5H), 6.78 (d, *J* = 3.2 Hz, 2H), 5.97 (d, *J* = 0.8 Hz, 1H), 5.16 (d, *J* = 0.8 Hz, 1H), 4.08 (s, 2H), 3.65 (s, 3H), 2.73 (d, *J* = 4.0 Hz, 1H), 2.32 (s, 1H), 1.87 (d, *J* = 4.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 150.8, 149.1, 143.5, 139.4, 130.8, 128.3, 127.5, 125.8, 121.9, 115.8, 115.2, 110.8, 65.9, 56.6, 23.1, 22.3. IR (neat) 3082, 2930, 2869, 1619, 1478, 1441, 1243, 1192, 1086, 1029, 954, 805, 705. HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{18}H_{19}O_2$: 267.1380; Found, 267.1378.



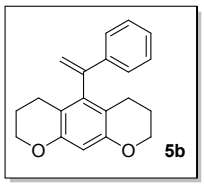
7-methoxy-6-(1-phenylvinyl)-2,3,4,5-tetrahydrobenzo[b]oxepine (3x): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.31-7.23 (m, 5H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 5.97 (t, *J* = 0.8 Hz, 1H), 5.11 (t, *J* = 0.8 Hz, 1H), 4.08-3.90 (m, 2H), 3.65 (s, 3H), 2.75-2.71 (m, 2H), 1.93-1.87 (m, 2H), 1.51 (d, *J* = 7.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.7, 153.1, 144.1, 140.0, 136.2, 130.6, 128.3, 128.2, 127.4, 126.6, 125.9, 120.3, 115.0, 108.9, 74.0, 56.2, 32.4, 29.5, 25.9. IR (neat) 3384, 2929, 2855, 1618, 1493, 1476, 1265, 1234, 1065, 999, 903, 780. HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{19}H_{21}O_2$: 281.1536; Found, 281.1532.

5. General procedure for the preparation of the products 5

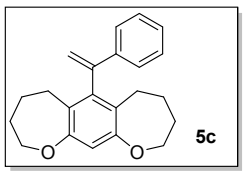
4 (0.2 mmol), **2** (0.4 mmol), $Pd(OAc)_2$ (4.5 mg,10 mol %), PPh_3 (10.5 mg, 20 mol %), norbornene (37.6 mg, 0.4 mmol, 2 equiv), Cs_2CO_3 (326 mg, 1 mmol, 5 equiv), H_2O (5equiv) were dissolved in 4 mL of degassed dry dioxane. The mixture was flushed with N_2 and stirred at room temperature for 15 minutes, then heated at 80 °C for 16 h. After cooling at room temperature, the mixture was diluted with diethyl ether, washed with water, dried over magnesium sufate, and purified by flash chromatography (silica, petroleum ether/AcOEt).



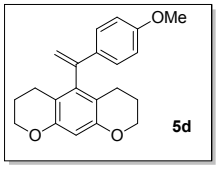
4-(1-phenylvinyl)-2,3,5,6-tetrahydrobenzo[1,2-b:5,4-b']difuran (5a): solid; m.p. 112-114 °C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.31 (s, 5H), 6.30 (s, 1H), 5.78 (d, *J* = 0.8 Hz, 1H), 5.27 (t, *J* = 0.8 Hz, 1H), 4.50 (t, *J* = 8.4 Hz, 4H), 2.83 (t, *J* = 8.4 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 160.3, 146.2, 139.4, 134.6, 128.4, 127.8, 126.6, 117.4, 115.1, 91.8, 72.1, 28.7. IR (neat) 3378, 2922, 2853, 1598, 1438, 1242, 1156, 1060, 781, 702. HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{18}H_{17}O_2$: 265.1223; Found, 265.1220.



5-(1-phenylvinyl)-2,3,4,6,7,8-hexahydropyrano[3,2-g]chromene (5b): solid; m.p.104-106 °C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.30-7.26 (m, 5H), 6.33 (s, 1H), 5.97 (s, 1H), 5.12 (s, 1H), 4.09 (m, 4H), 2.70-2.62 (m, 2H), 2.28-2.21 (m, 2H), 1.90-1.82 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.8, 145.3, 141.8, 138.7, 128.5, 127.8, 125.6, 114.6, 113.2, 103.3, 66.1, 22.6. IR (neat) 3379, 2923, 2376, 1594, 1461, 1260, 1105, 800, 619. HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{20}H_{21}O_2$: 293.1536; Found, 293.1534.



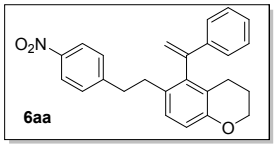
6-(1-phenylvinyl)-2,3,4,5,7,8,9,10-octahydrobenzo[1,2-b:5,4-b']bis(oxepine) (5c): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.28 (d, *J* = 5.6 Hz, 5H), 6.70 (s, 1H), 5.96 (s, 1H), 5.05 (s, 1H), 4.06-3.92 (m, 4H), 2.67-2.62 (m, 4H), 1.90-1.84 (m, 4H), 1.44-1.41 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.2, 146.9, 141.2, 139.9, 129.6, 128.4, 128.3, 127.7, 126.6, 126.1, 114.2, 113.3, 73.8, 32.3, 29.7, 25.9. IR (neat) 3371, 2923, 2853, 1738, 1588, 1462, 1376, 1160, 1113, 1033, 786. HRMS-ESI (m/z) [M + H]$^+$ calcd for $C_{22}H_{25}O_2$: 321.1849; Found, 321.1845.



5-(1-(4-methoxyphenyl)vinyl)-2,3,4,6,7,8-hexahydropyrano[3,2-g]chromene (5d): solid; m.p. 121-123 °C; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 7.22 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.32 (s, 1H), 5.85 (d, *J* = 0.8 Hz, 1H), 5.00 (d, *J* = 8.8 Hz, 1H), 4.13-4.05 (m, 4H), 3.80 (s, 3H), 2.70-2.62 (m, 2H), 2.29-2.22 (m, 2H), 1.91-1.80 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 159.3, 153.7, 144.7, 142.1, 131.2, 126.8, 113.8, 113.1, 112.4, 103.1, 66.2, 55.2, 22.7, 22.6. IR (neat) 3379, 2925, 2375, 1603, 1461, 1249, 1135, 1032, 839. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{21}H_{23}O_3$: 323.1642; Found, 323.1637.

6. General procedure for the preparation of the product 6aa

1t (0.2 mmol), **2a** (0.4 mmol), **6a** (0.6 mmol), $Pd(OAc)_2$ (4.5 mg,10 mol %), PPh_3 (10.5 mg, 20 mol %), norbornene (37.6 mg, 0.4 mmol, 2 equiv), Cs_2CO_3 (326 mg, 1 mmol, 5 equiv), H_2O (5equiv) were dissolved in 4 mL of degassed dry dioxane. The mixture was flushed with N_2 and stirred at room temperature for 15 minutes, then heated at 80 °C for 16 h. After cooling at room temperature, the mixture was diluted with diethyl ether, washed with water, dried over magnesium sufate, and purified by flash chromatography (silica, petroleum ether/AcOEt).



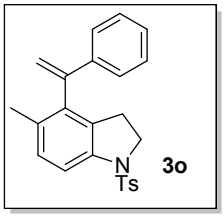
6-(4-nitrophenethyl)-5-(1-phenylvinyl)chroman (6aa): oil; ^{1}H NMR ($CDCl_3$, 400MHz) δ: 8.04 (d, *J* = 8.4 Hz, 2H), 7.29-7.26 (m, 5H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.4 Hz, 1H), 6.01 (d, *J* = 0.8 Hz, 1H), 5.06 (d, *J* = 0.8 Hz, 1H), 4.17-4.08 (m, 2H), 2.86-2.68 (m, 5H), 2.38-2.30 (m, 1H), 1.94-1.88 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 153.4, 150.0, 146.2, 145.6, 141.1, 139.1, 132.3, 130.3, 129.2, 128.6, 128.4, 128.0, 127.6, 125.8, 123.5, 120.8, 116.0, 114.8, 66.0, 38.0, 34.5, 23.3, 22.4. IR (neat) 3404, 3079, 2929, 2862, 1598, 1517, 1345, 1192, 1106, 954, 909, 735. HRMS-ESI (m/z) $[M + H]^+$ calcd for $C_{25}H_{24}O_3N$: 386.1751; Found, 386.1743.

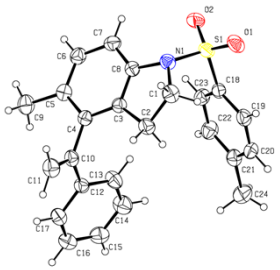
7. References:

(1) Fulton, J. R.; Aggarwal,V. K.; de Vicente, J. Eur. J. Org. Chem. 2005, 1479.

(2) (a) Mariampillai, B.; Alberico, D.; Bidau, V.; Lautens, M.; J. Am. Chem. Soc. 2006, 128, 14436. (b) Pache, S.; Lautens, M. Org. Lett. 2003, 5, 4827.

8. Crystallographic data of 3o





Structure of 3o

Datablock:

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	alpha=90	beta=96.402(5)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	2027.22(17)	2027.24(17)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C24 H23 N O2 S	C24 H23 N O2 S	
Sum formula	C24 H23 N O2 S	C24 H23 N O2 S	
Mr	389.50	389.49	
Dx,g cm-3	1.276	1.276	
Z	4	4	
Mu (mm-1)	0.179	0.179	
F000	824.0	824.0	
F000’	824.82		
h,k,lmax	14,10,25	14,10,25	
Nref	3992	3987	
Tmin,Tmax	0.950,0.960	0.543,1.000	
Tmin’	0.919		

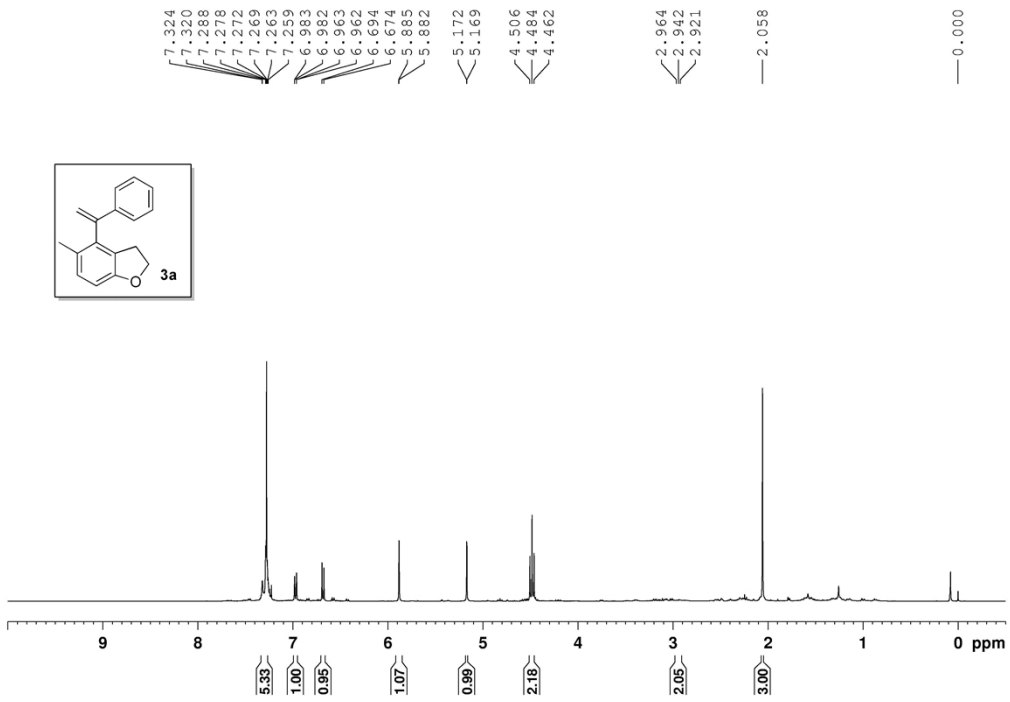
Correction method= MULTI-SCAN

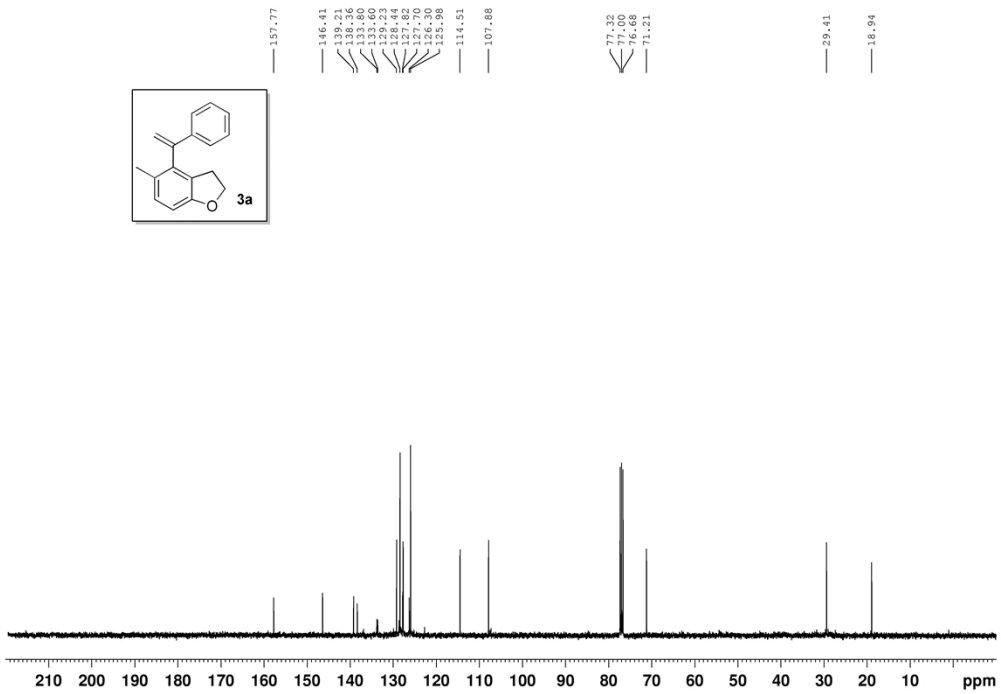
Data completeness= 0.999 Theta(max)= 26.022

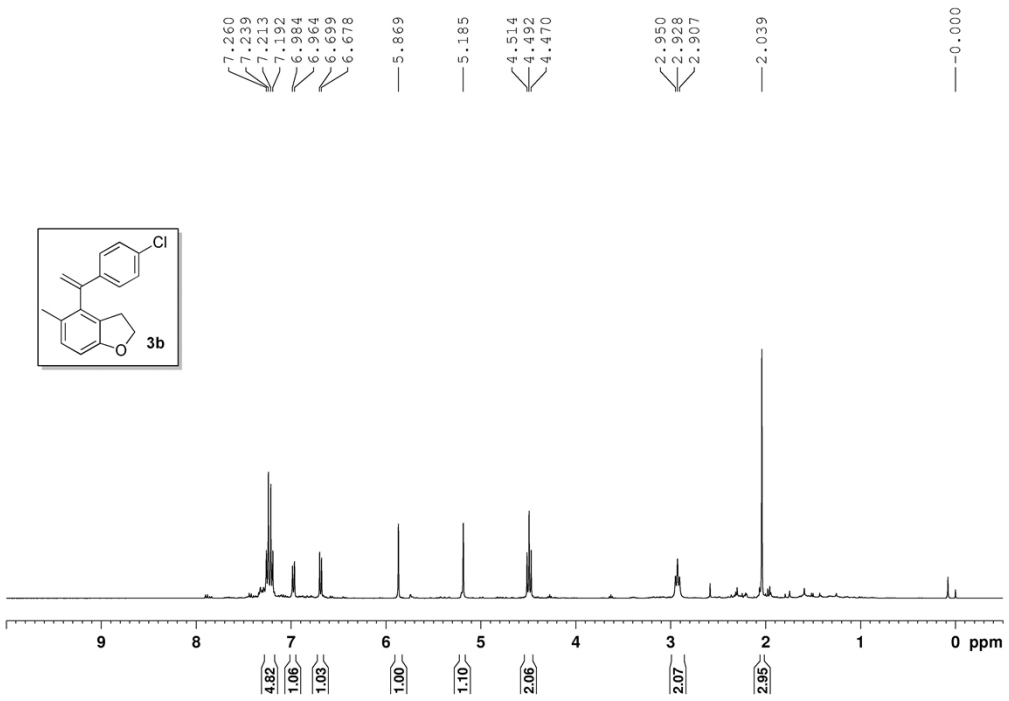
R(reflections)= 0.0552(2557) wR2(reflections)= 0.1445(3987)

S = 1.061 Npar= 264

9. ^{1}H NMR, ^{13}C NMR Spectra for products 3a-3x, 5a-5d and 6aa



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2.907
2.039
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Cl
3b
9
8
7
6
5
4
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2
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1.00
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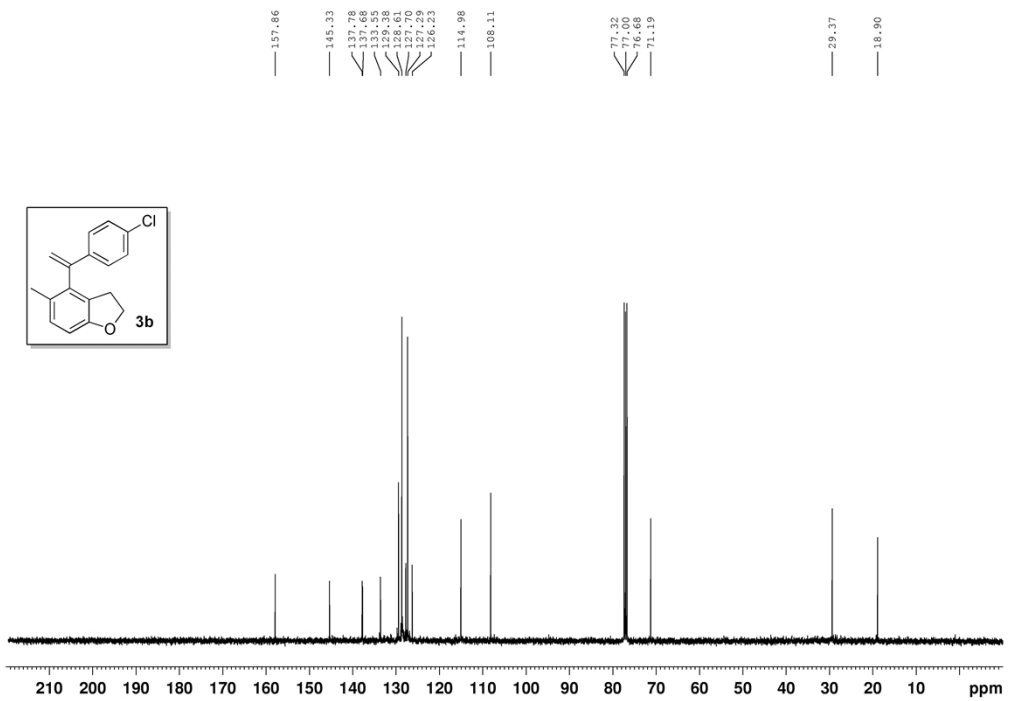
2.95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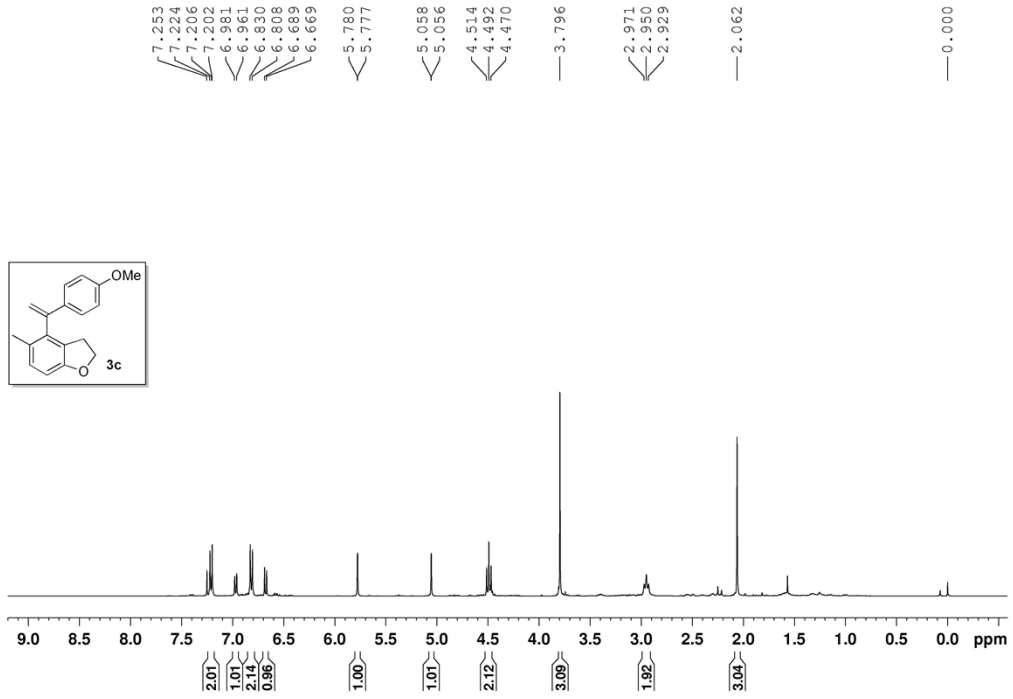
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2.971
2.950
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OMe
3c
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
2.01
1.01
2.14
0.96
1.00
1.01
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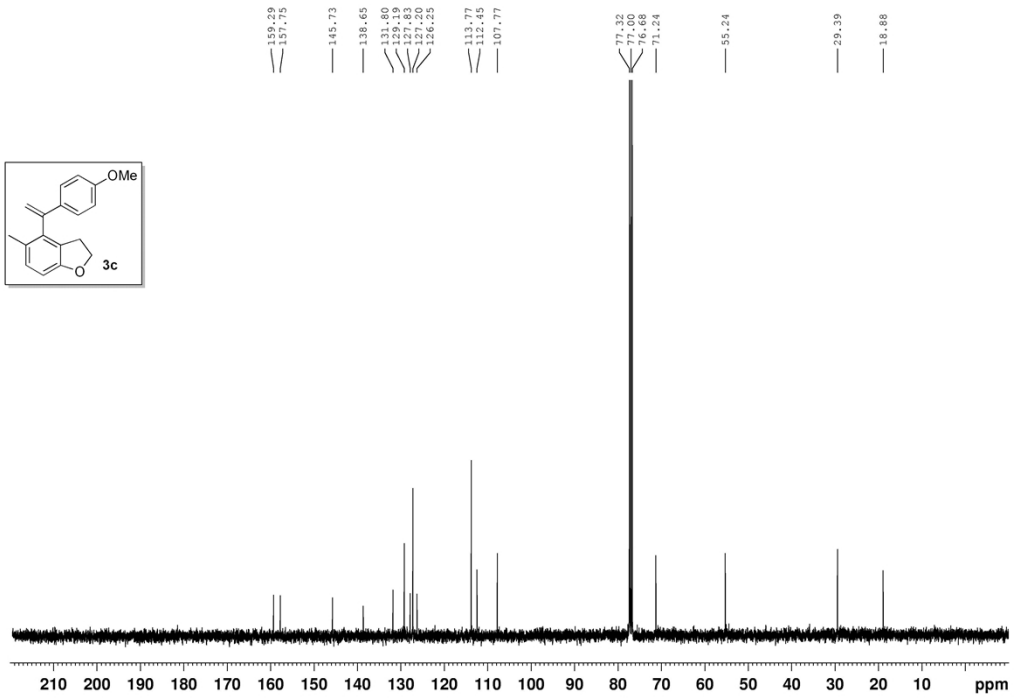
3.09
1.92
3.04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138.65
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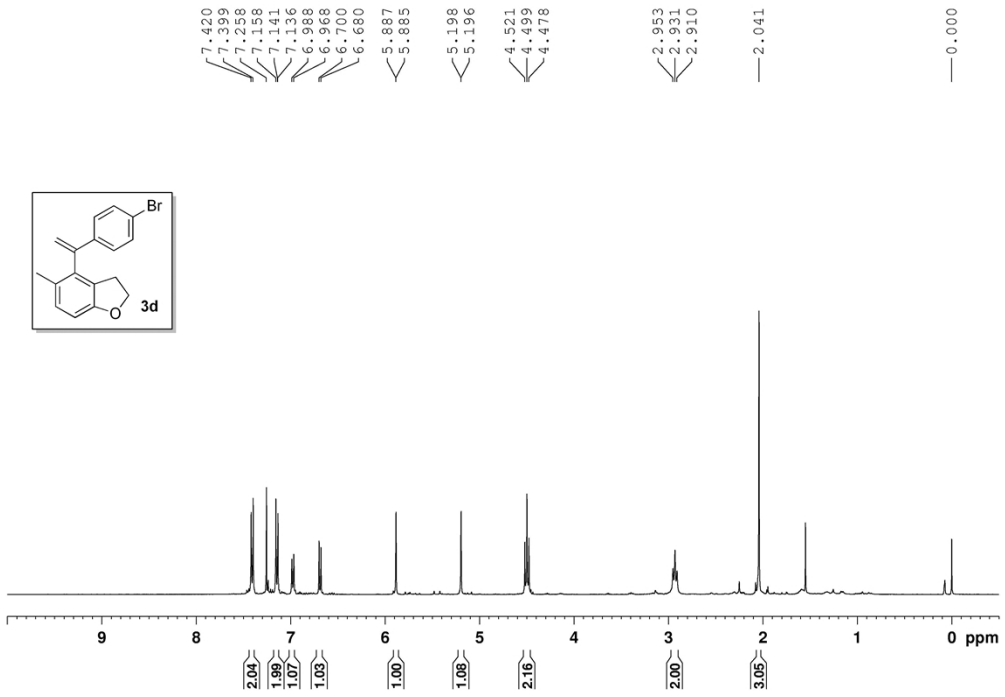
129.19
127.83
127.20
126.25
113.77
112.45
107.77
77.32
77.00
76.68
71.24
55.24
29.39
18.88
OMe
3c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.399
7.258
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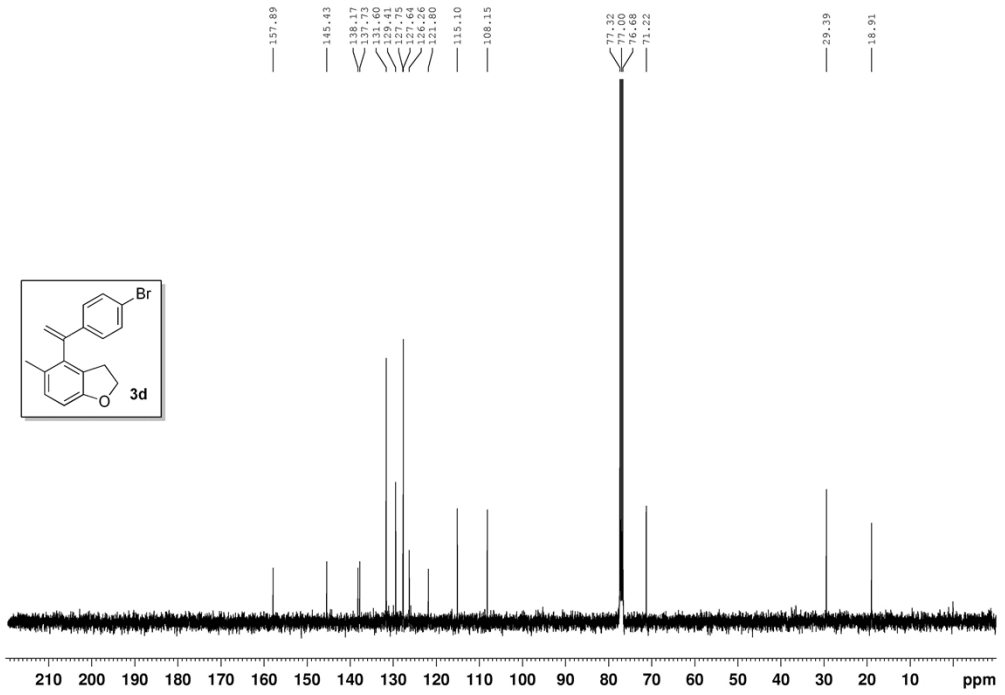
7.141
7.136
6.988
6.968
6.700
6.680
5.887
5.885
5.198
5.196
4.521
4.499
4.478
2.953
2.931
2.910
2.041
0.000
Br
3d
9
8
7
6
5
4
3
2
1
0 ppm
2.04
1.99
1.07
1.03
1.00
1.08
2.16
2.00
3.05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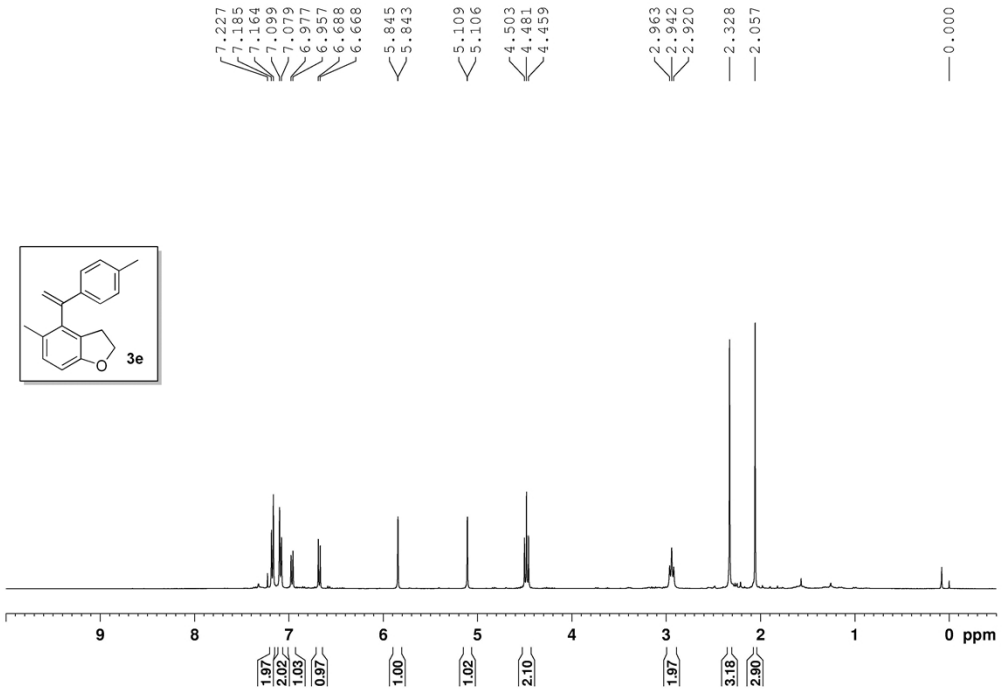
138.17
137.73
131.60
129.41
129.15
127.64
126.26
121.80
115.10
108.15
77.32
77.00
76.68
71.22
29.39
18.91
Br
3d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.079
6.977
6.957
6.688
6.668
5.845
5.843
5.109
5.106
4.503
4.481
4.459
2.963
2.942
2.920
2.328
2.057
0.000
3e
9
8
7
6
5
4
3
2
1
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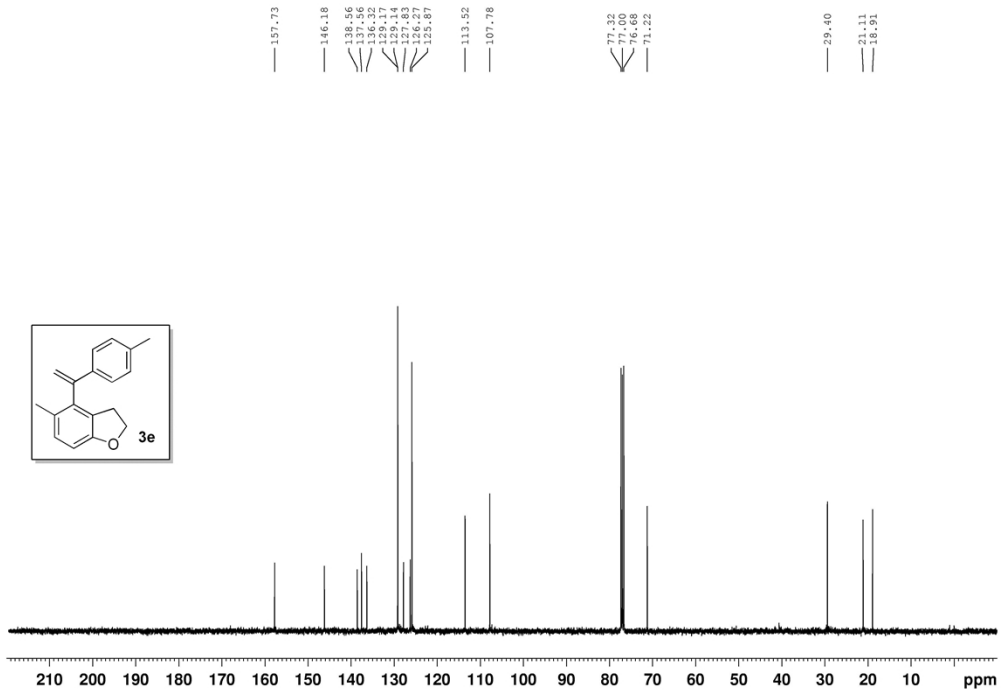
1.97
2.02
1.03
0.97
1.00
1.02
2.10
1.97
3.18
2.90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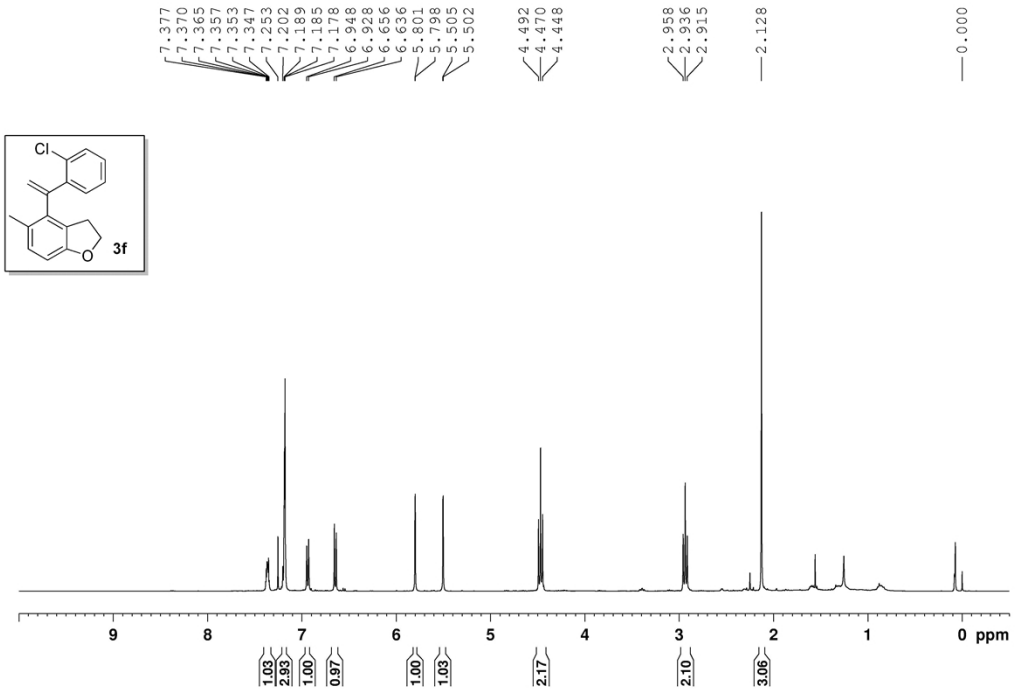
127.83
126.27
125.87
113.52
107.78
77.32
77.00
76.68
71.22
29.40
21.11
18.91
3e
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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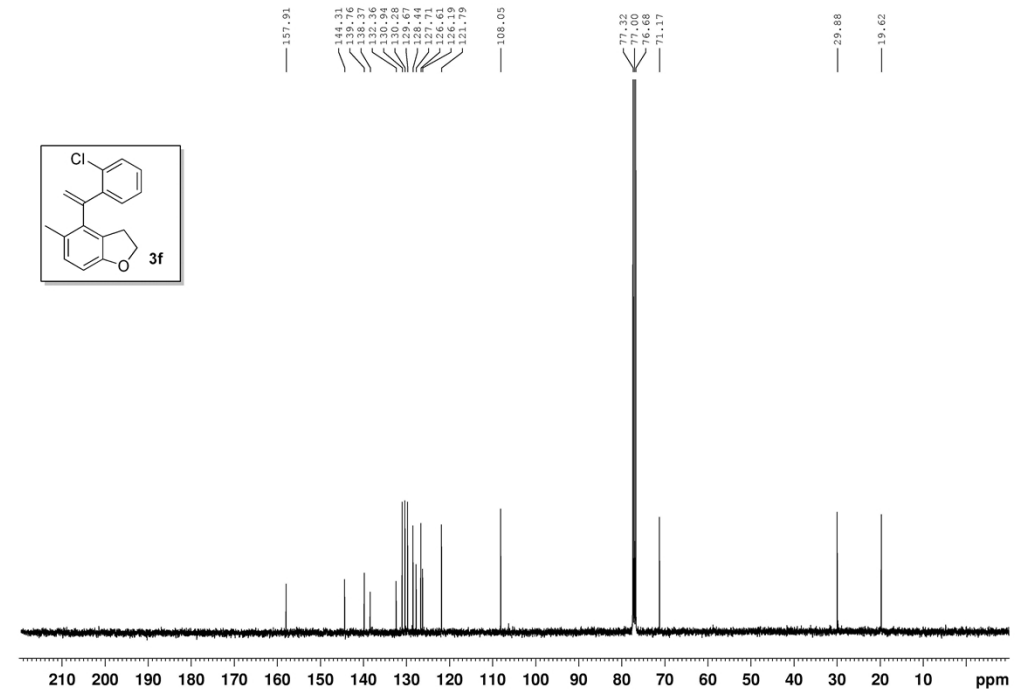
7.370
7.365
7.357
7.353
7.347
7.253
7.202
7.189
7.185
7.178
6.948
6.928
6.656
6.636
5.801
5.798
5.505
5.502
4.492
4.470
4.448
2.958
2.936
2.915
2.128
0.000
Cl
O
3f
9
8
7
6
5
4
3
2
1
0 ppm
1.03
2.93
1.00
0.97
1.00
1.03
2.17
2.10
3.06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139.76
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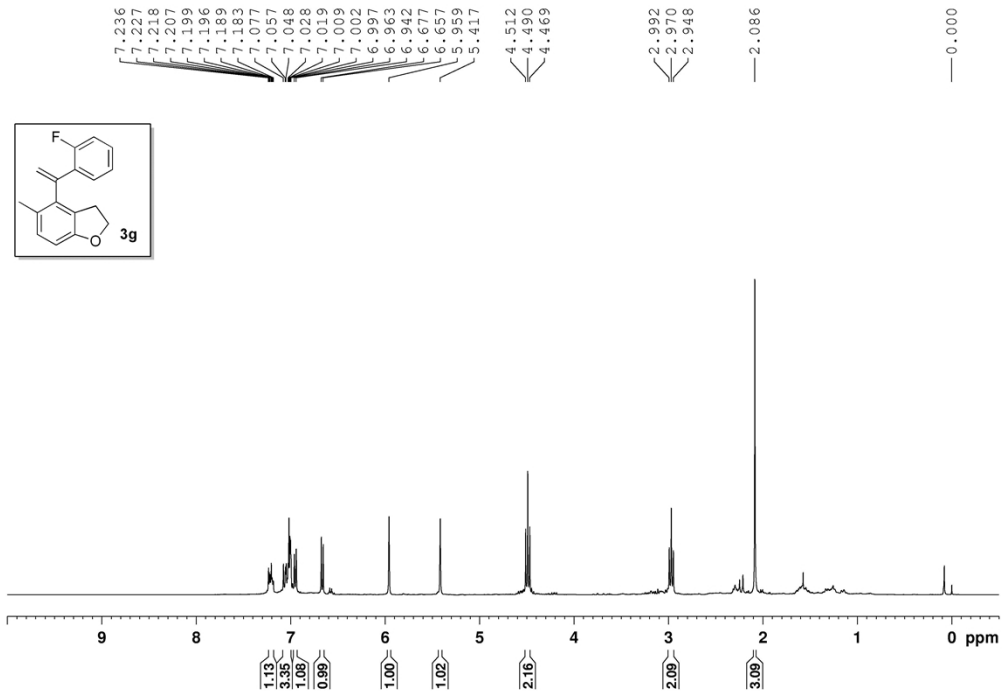
132.96
130.84
130.28
129.67
128.44
127.71
126.61
126.19
121.79
108.05
77.32
77.00
76.68
71.17
29.88
19.62
Cl
O
3f
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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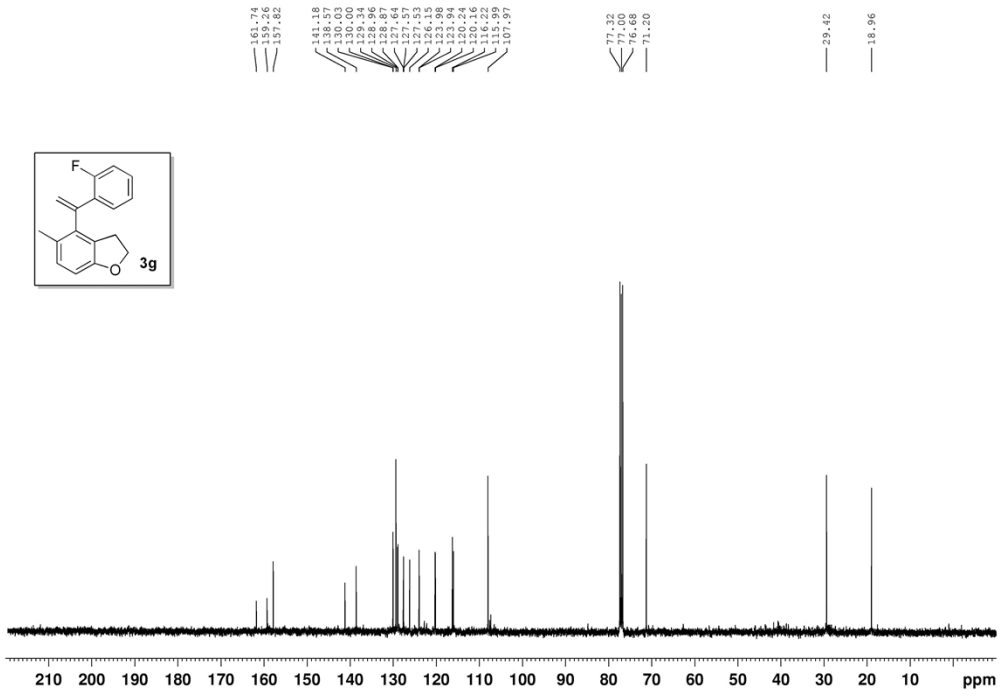
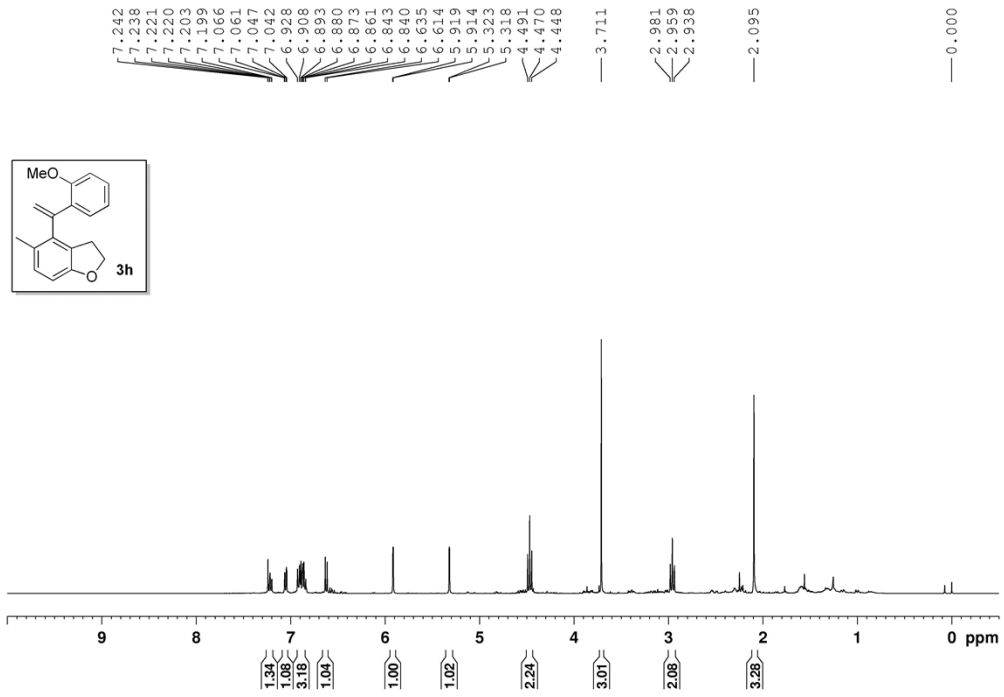
7.227
7.218
7.207
7.199
7.196
7.189
7.183
7.077
7.057
7.048
7.028
7.019
7.009
7.002
6.997
6.963
6.942
6.677
6.657
5.959
5.417
4.512
4.490
4.469
2.992
2.970
2.948
2.086
0.000
F
3g
9
8
7
6
5
4
3
2
1
0 ppm
1.13
3.35
1.08
0.99
1.00
1.02
2.16
2.09
3.09


161.74
159.26
157.82
141.18
138.57
130.03
130.00
129.34
128.86
128.87
127.64
127.57
127.53
123.15
123.98
123.94
120.24
120.16
116.22
116.09
107.97
77.32
77.00
76.68
71.20
29.42
18.96
F
3g
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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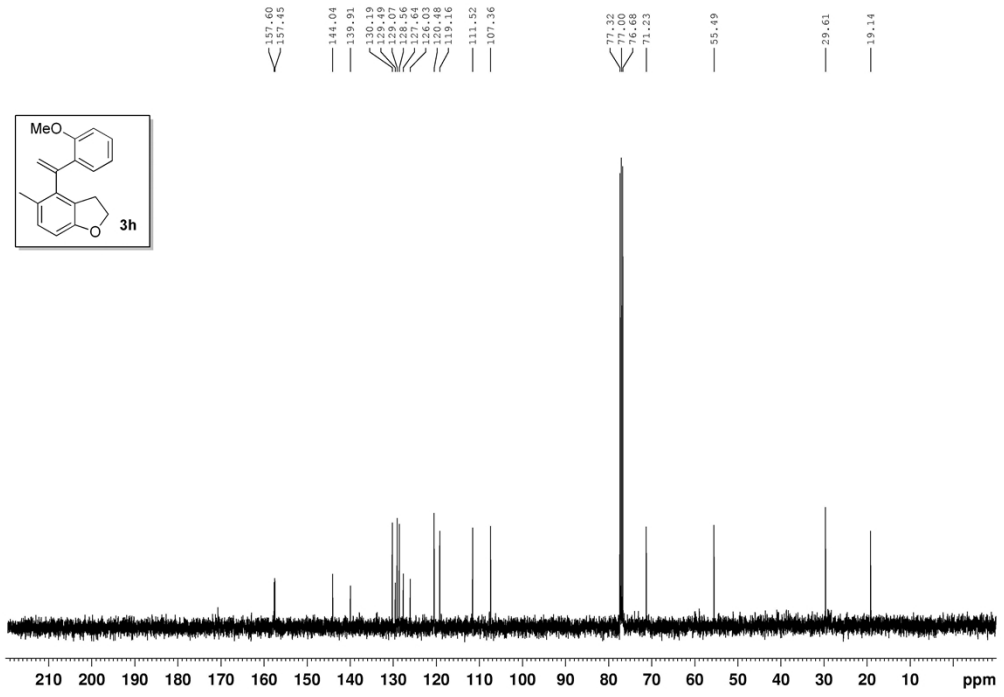
7.238
7.221
7.220
7.203
7.199
7.066
7.061
7.047
7.042
6.928
6.908
6.893
6.880
6.873
6.861
6.843
6.840
6.635
6.614
5.919
5.914
5.323
5.318
4.491
4.470
4.448
3.711
2.981
2.959
2.938
2.095
0.000
MeO
3h
9
8
7
6
5
4
3
2
1
0 ppm
1.34
1.08
3.18
1.04
1.00
1.02
2.24
3.01
2.08
3.28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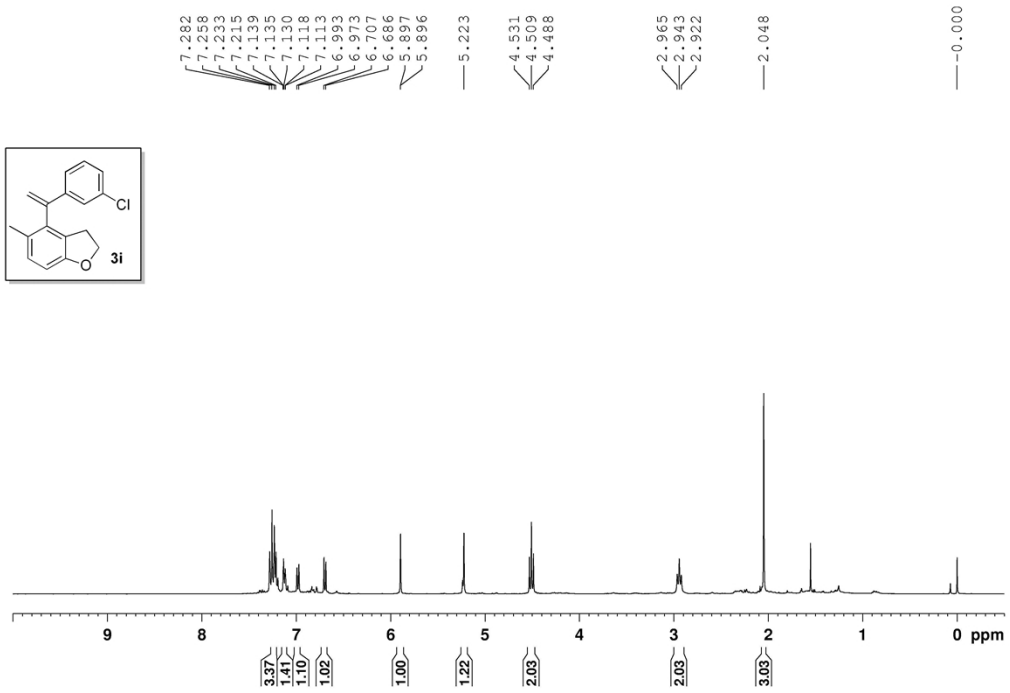
157.45
144.04
139.91
130.19
129.49
129.07
128.56
127.64
126.03
120.48
119.16
111.52
107.36
77.32
77.00
76.68
71.23
55.49
29.61
19.14
MeO
3h
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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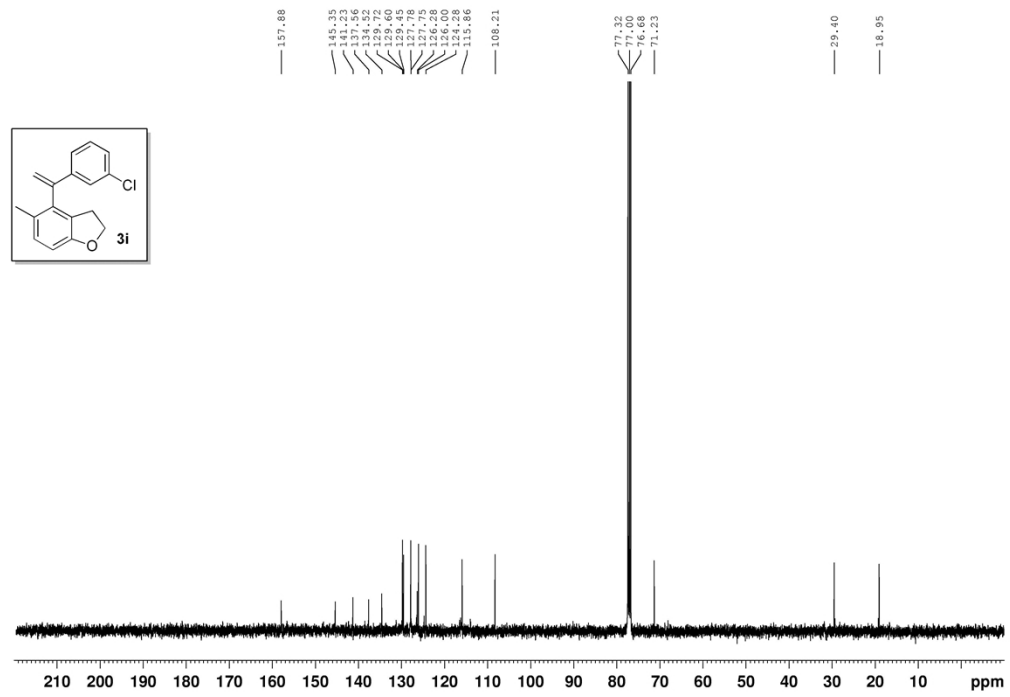
7.135
7.130
7.118
7.113
6.993
6.973
6.707
6.686
5.897
5.896
5.223
4.531
4.509
4.488
2.965
2.943
2.922
2.048
0.000
Cl
O
3i
9
8
7
6
5
4
3
2
1
0 ppm
3.37
1.41
1.10
1.02
1.00
1.22
2.03
2.03
3.03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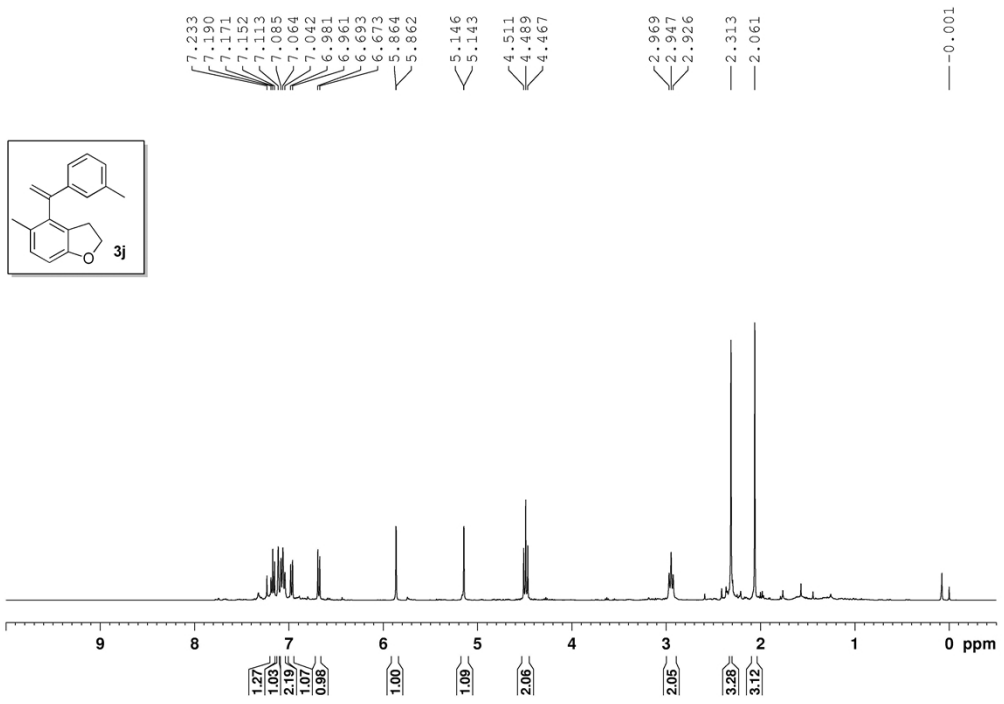
141.23
137.56
134.22
129.72
129.60
129.45
127.78
127.75
126.28
126.00
124.28
115.86
108.21
77.32
77.00
76.68
71.23
29.40
18.95
Cl
O
3i
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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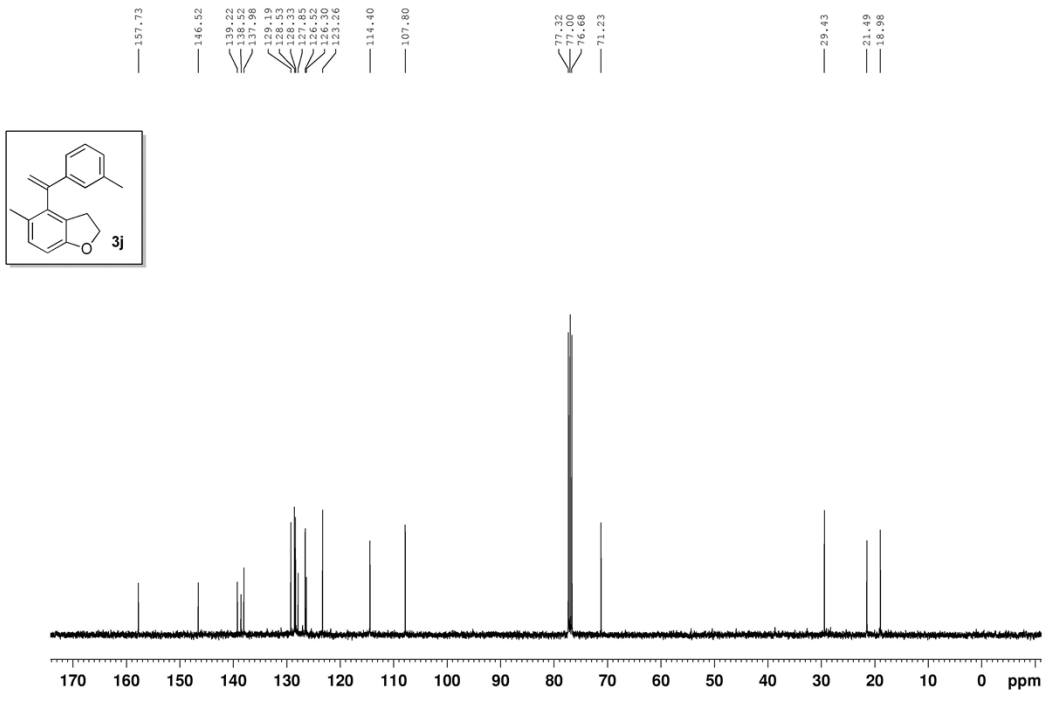
7.190
7.171
7.152
7.113
7.085
7.064
7.042
6.981
6.961
6.693
6.673
5.864
5.862
5.146
5.143
4.511
4.489
4.467
2.969
2.947
2.926
2.313
2.061
-0.001
3j
9
8
7
6
5
4
3
2
1
0 ppm
1.27
1.03
2.19
1.07
0.98
1.00
1.09
2.06
2.05
3.28
3.12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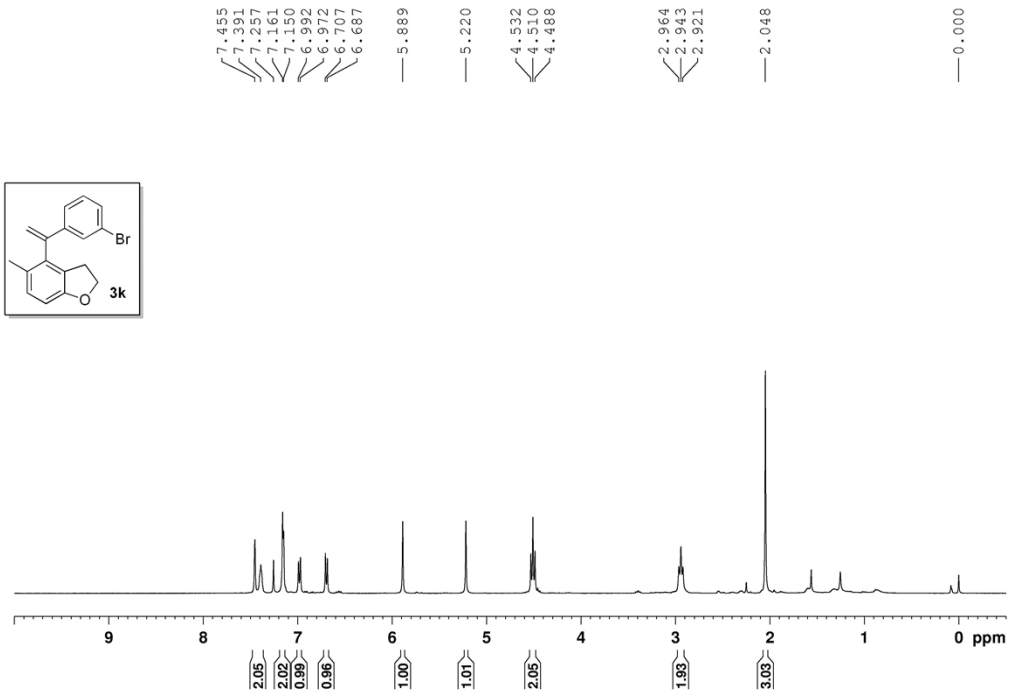
137.98
129.19
128.53
128.23
127.85
126.52
126.30
123.26
114.40
107.80
77.32
77.00
76.68
71.23
29.43
21.49
18.98
3j
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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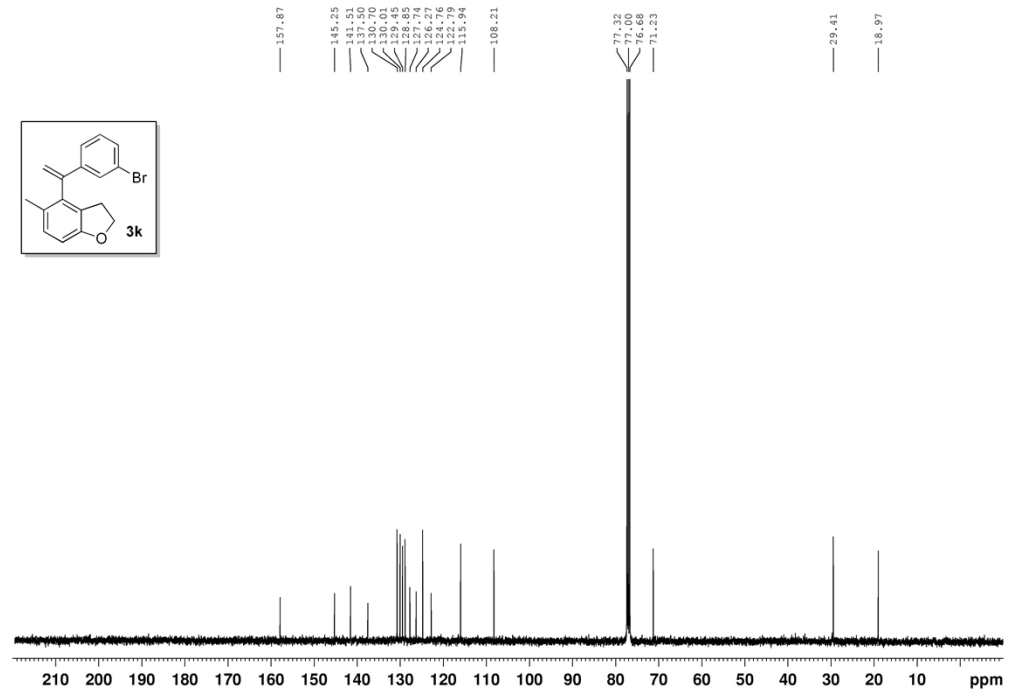
6.972
6.707
6.687
5.889
5.220
4.532
4.510
4.488
2.964
2.943
2.921
2.048
0.000
Br
3k
9
8
7
6
5
4
3
2
1
0 ppm
2.05
2.02
0.99
0.96
1.00
1.01
2.05
1.93
3.03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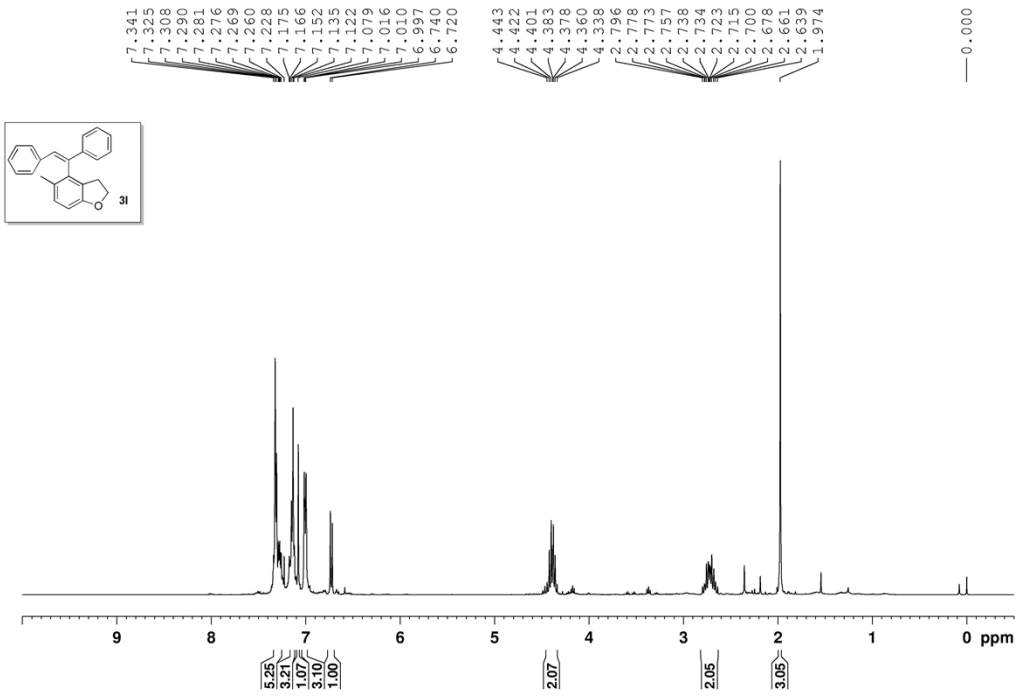
130.01
129.45
128.55
127.74
126.27
124.76
122.79
115.94
108.21
77.32
77.00
76.68
71.23
29.41
18.97
Br
3k
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.276
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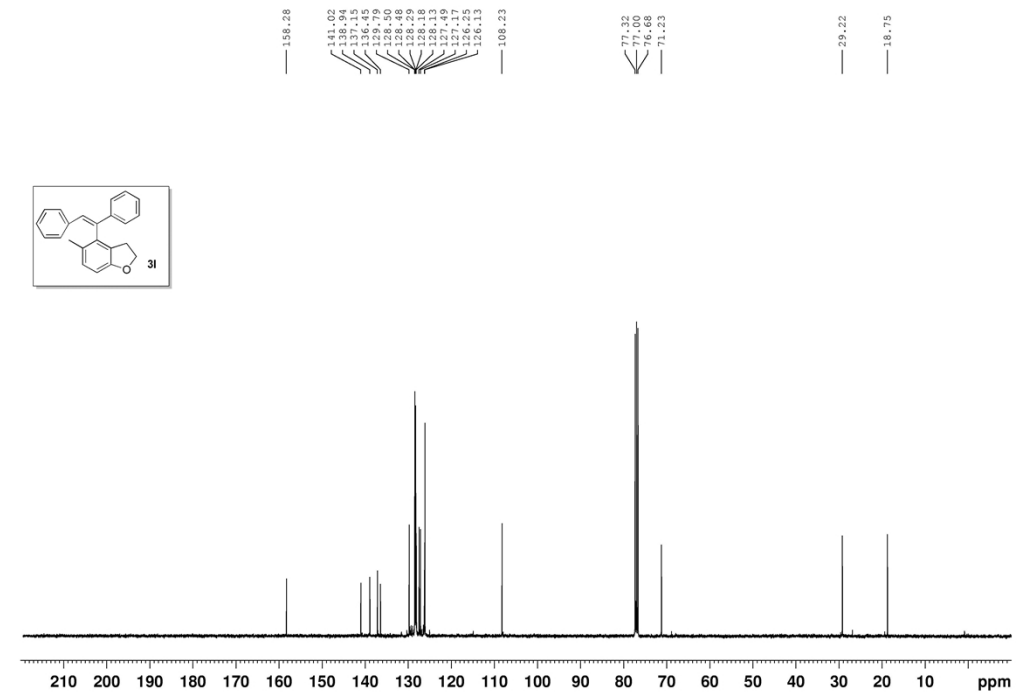
7.260
7.228
7.175
7.166
7.152
7.135
7.122
7.079
7.016
7.010
6.997
6.740
6.720
4.443
4.422
4.401
4.383
4.378
4.360
4.338
2.796
2.778
2.773
2.757
2.738
2.734
2.723
2.715
2.700
2.678
2.661
2.639
1.974
0.000
3l
9
8
7
6
5
4
3
2
1
0 ppm
5.25
3.21
1.07
3.10
1.00
2.07
2.05
3.05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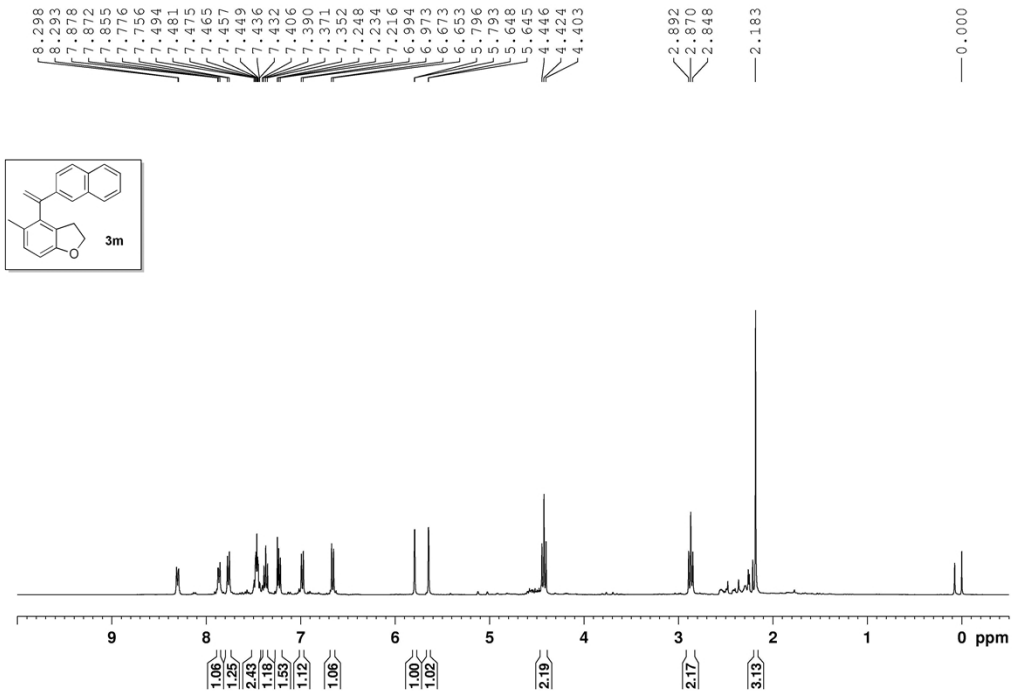
138.94
137.15
136.45
129.79
128.40
128.40
128.29
128.18
128.13
127.49
127.17
126.25
126.13
108.23
77.32
77.00
76.68
71.23
29.22
18.75
3l
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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7.776
7.756
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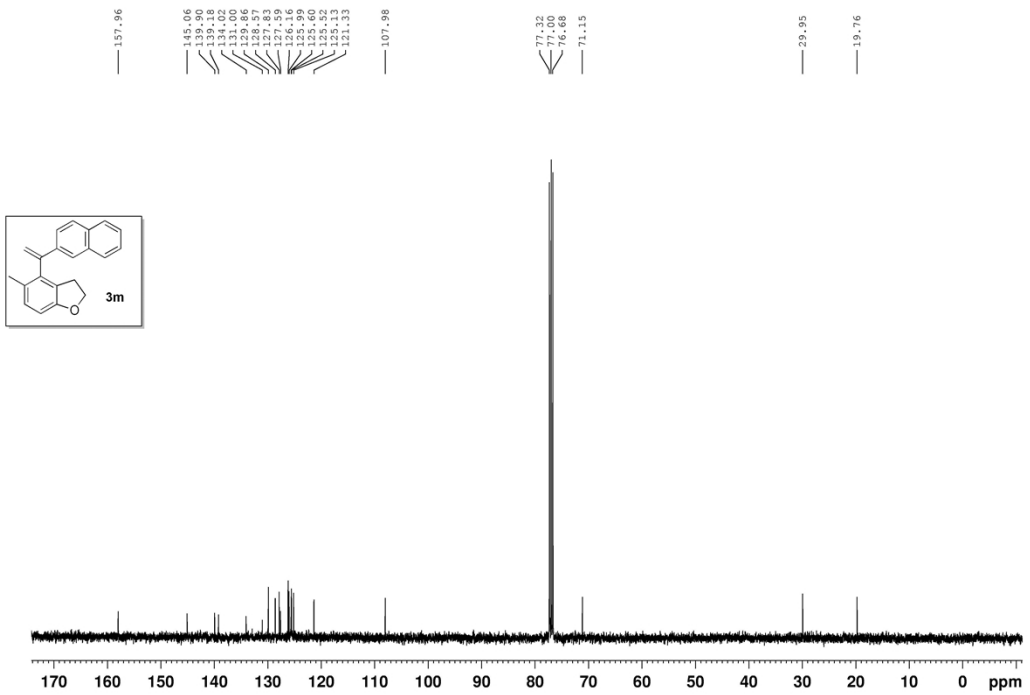
7.481
7.475
7.465
7.457
7.449
7.436
7.432
7.406
7.390
7.371
7.352
7.248
7.234
7.216
6.994
6.973
6.673
6.653
5.796
5.793
5.648
5.645
4.446
4.424
4.403
2.892
2.870
2.848
2.183
0.000
3m
9
8
7
6
5
4
3
2
1
0 ppm
1.06
1.25
2.43
1.18
1.53
1.12
1.06
1.00
1.02
2.19
2.17
3.13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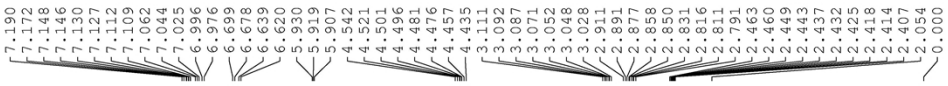
145.06
139.90
139.18
134.02
131.00
129.66
128.57
127.83
127.59
126.16
125.89
125.60
125.52
125.13
121.33
107.98
77.32
77.00
76.68
71.15
29.95
19.76
3m
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm


7.190
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7.146
7.130
7.127
7.112
7.109
7.062
7.044
7.025
6.996
6.976
6.699
6.678
6.639
6.620
5.930
5.919
5.907
4.542
4.521
4.501
4.496
4.481
4.476
4.457
4.435
3.111
3.092
3.087
3.071
3.052
3.048
3.028
2.911
2.891
2.877
2.858
2.850
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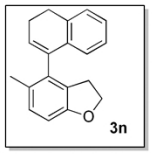
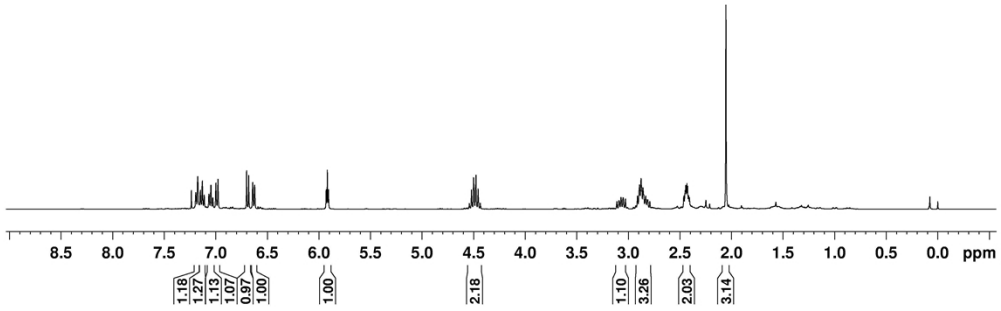
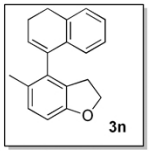
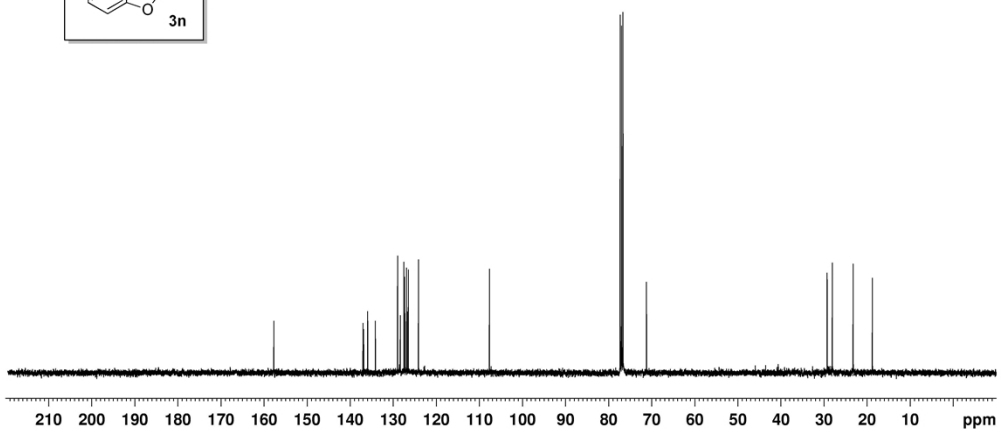
2.054
0.000

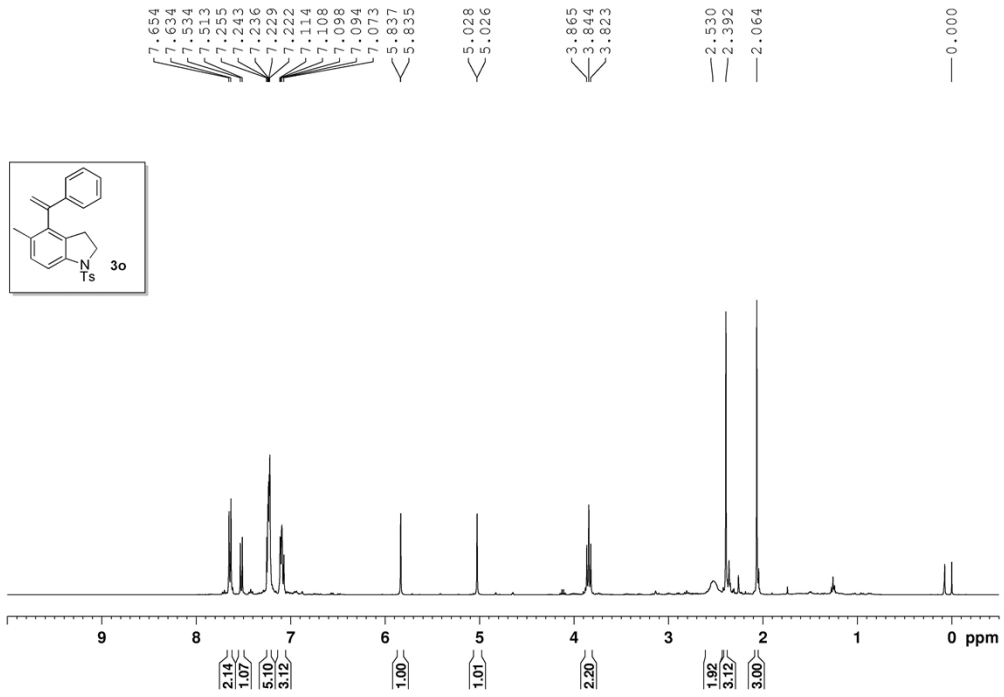

3n


8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
1.18
1.27
1.13
1.07
0.97
1.00
1.00
2.18
1.10
3.26
2.03
3.14


157.73
137.03
136.88
135.95
134.15
129.00
128.37
127.32
127.36
126.94
126.68
126.52
124.15
107.68
77.32
77.00
76.68
71.23
29.27
28.08
23.24
18.78


3n


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm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7.094
7.073
5.837
5.835
5.028
5.026
3.865
3.844
3.823
2.530
2.392
2.064
0.000
N
Ts
3o
9
8
7
6
5
4
3
2
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1.07
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1.01
2.20
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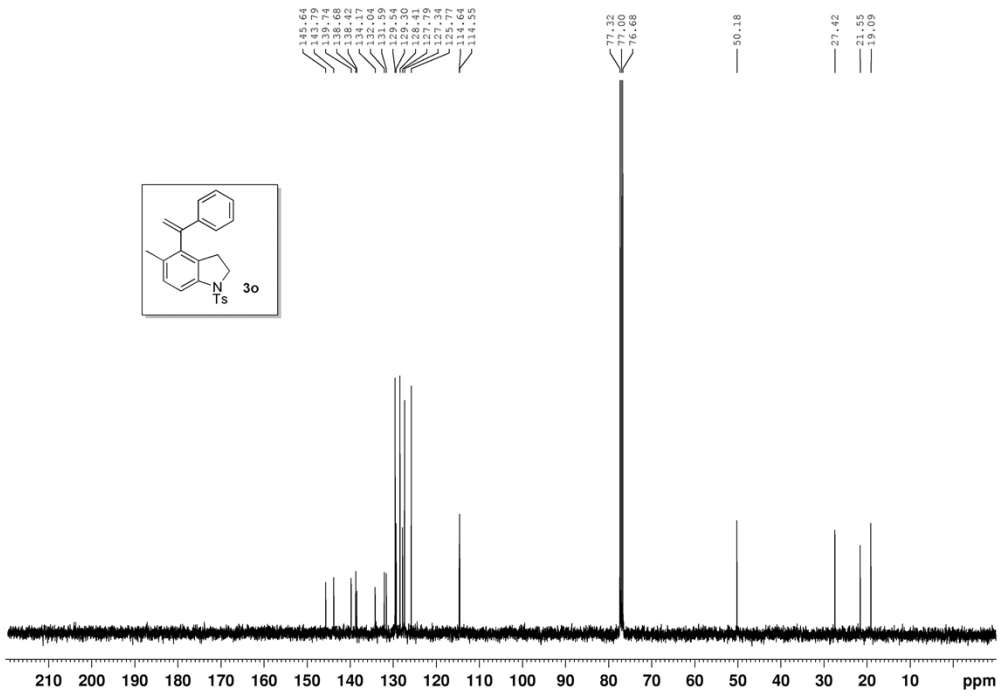
3.00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127.89
127.34
125.77
114.64
114.55
77.32
77.00
76.68
50.18
27.42
21.55
19.09
N
Ts
3o
210
200
190
180
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150
140
130
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110
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90
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70
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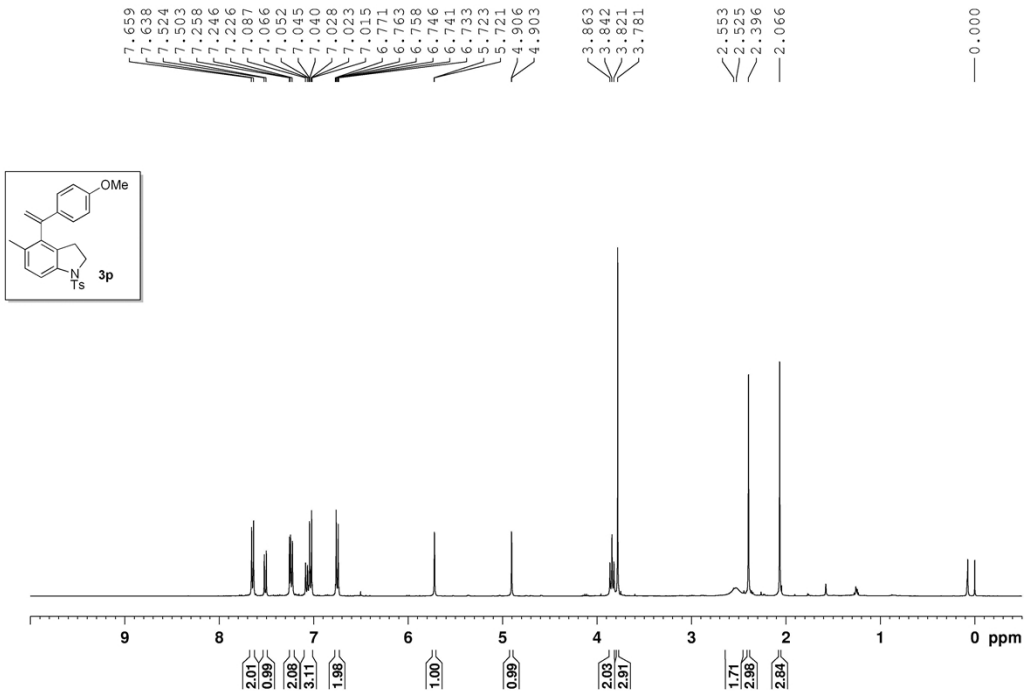
30
20
10
ppm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7.028
7.023
7.015
6.771
6.763
6.758
6.746
6.741
6.733
5.723
5.721
4.906
4.903
3.863
3.842
3.821
3.781
2.553
2.525
2.396
2.066
0.000
OMe
N
Ts
3p
9
8
7
6
5
4
3
2
1
0 ppm
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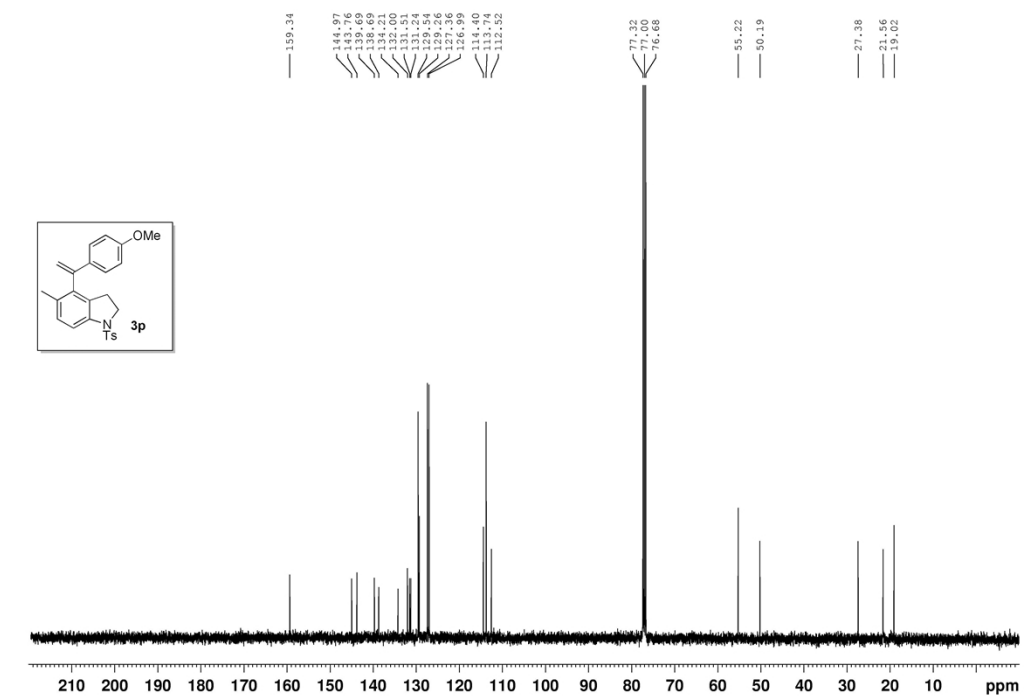
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131.51
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129.26
127.06
126.99
114.40
113.74
112.52
77.32
77.00
76.68
55.22
50.19
27.38
21.56
19.02
OMe
N
Ts
3p
210
200
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150
140
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20
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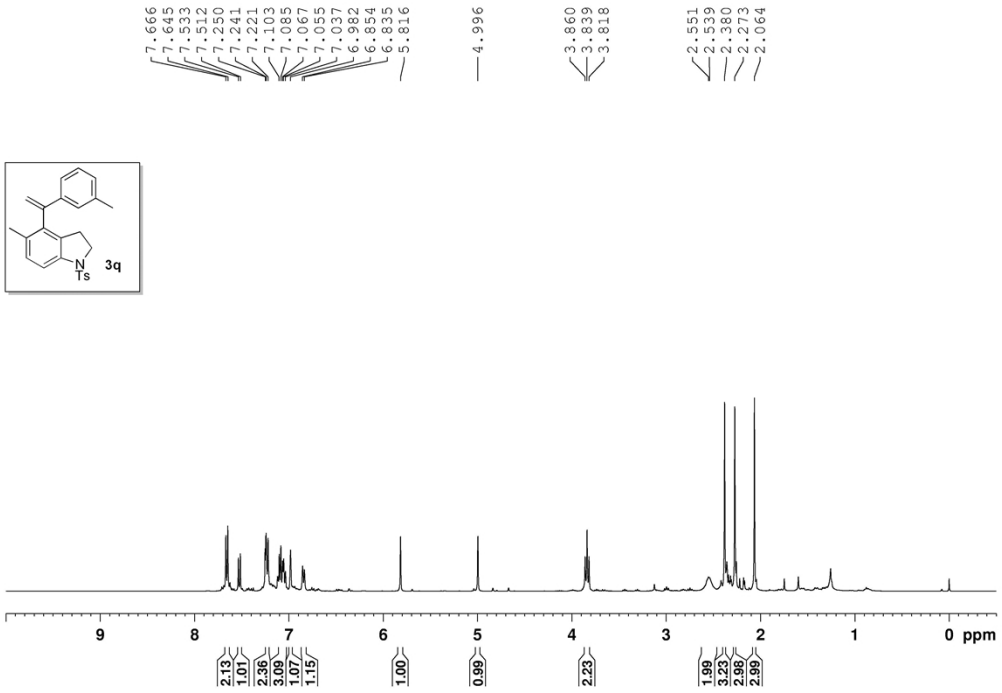
ppm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7.037
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6.854
6.835
5.816
4.996
3.860
3.839
3.818
2.551
2.539
2.380
2.273
2.064
3q
9
8
7
6
5
4
3
2
1
0 ppm
2.13
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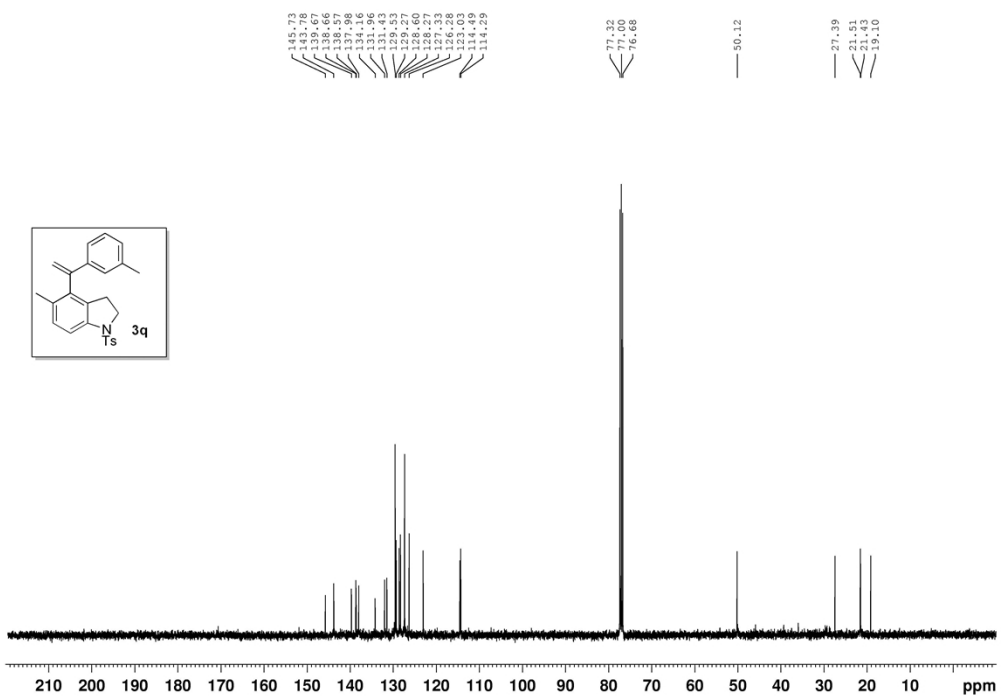
2.99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131.96
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129.53
129.27
128.60
128.37
127.33
126.28
123.03
114.49
114.29
77.32
77.00
76.68
50.12
27.39
21.51
21.43
19.10
3q
210
200
190
180
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150
140
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120
110
100
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80
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60
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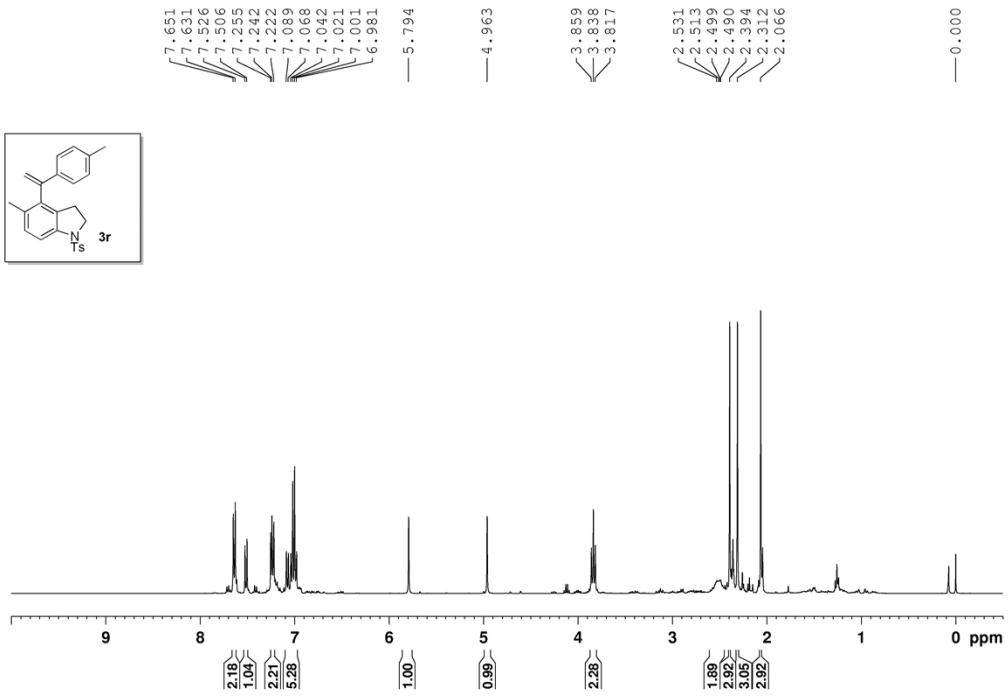
30
20
10
ppm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7.089
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7.021
7.001
6.981
5.794
4.963
3.859
3.838
3.817
2.531
2.513
2.499
2.490
2.394
2.312
2.066
0.000
3r
9
8
7
6
5
4
3
2
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2.21
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2.28
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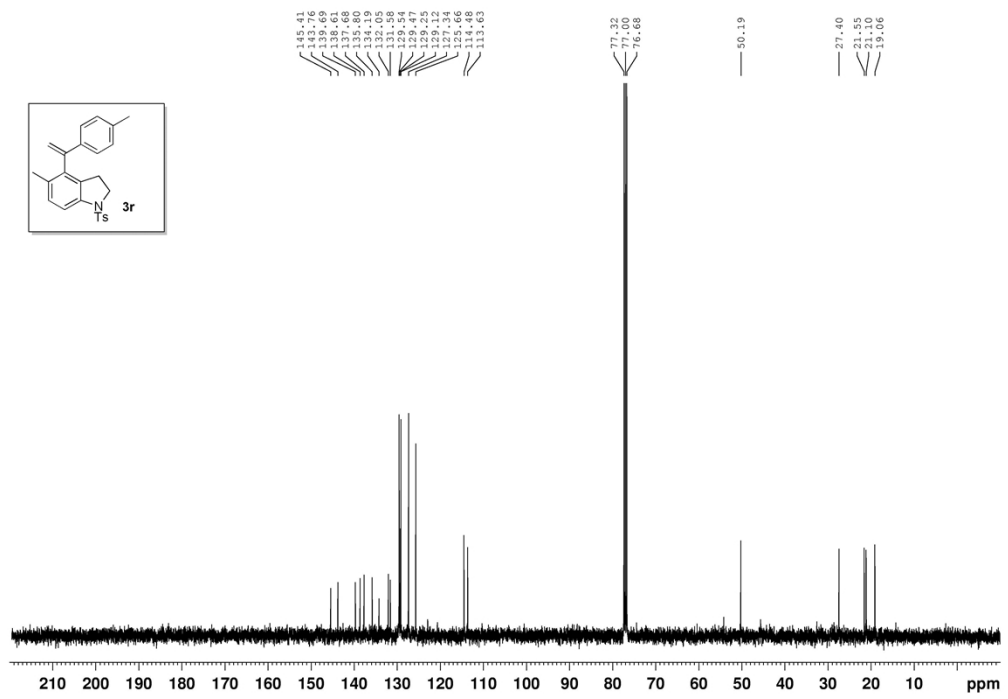
3.05
2.92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129.25
129.12
129.04
127.46
114.48
113.63
77.32
77.00
76.68
50.19
27.40
21.55
21.10
19.06
3r
210
200
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150
140
130
120
110
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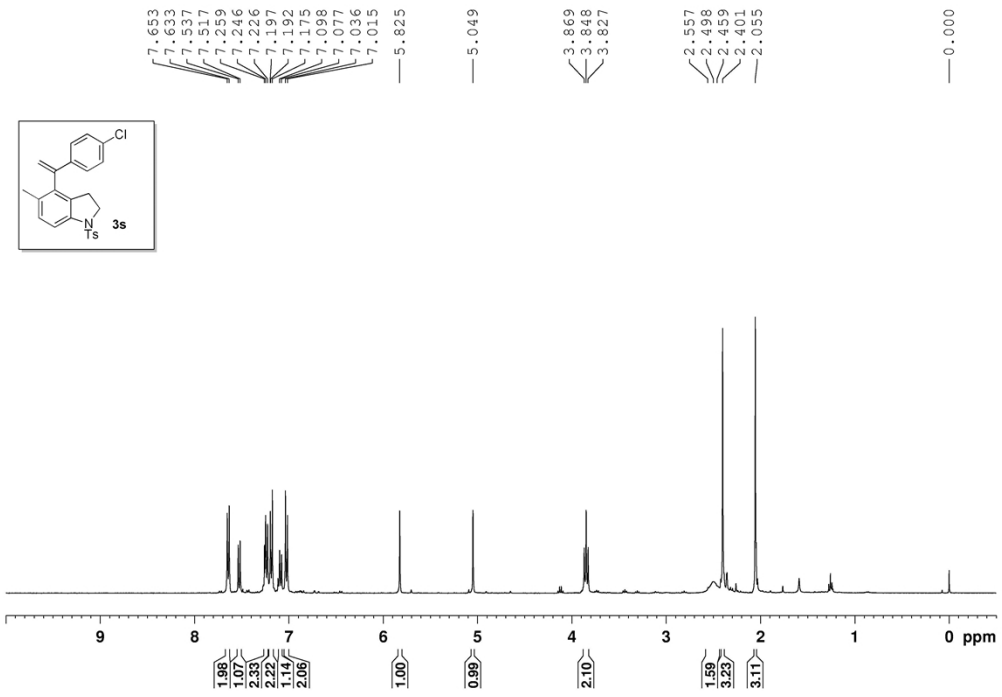
30
20
10
ppm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7.192
7.175
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7.077
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7.015
5.825
5.049
3.869
3.848
3.827
2.557
2.498
2.459
2.401
2.055
0.000
Cl
N
Ts
3s
9
8
7
6
5
4
3
2
1
0 ppm
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1.07
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2.22
1.14
2.06
1.00
0.99
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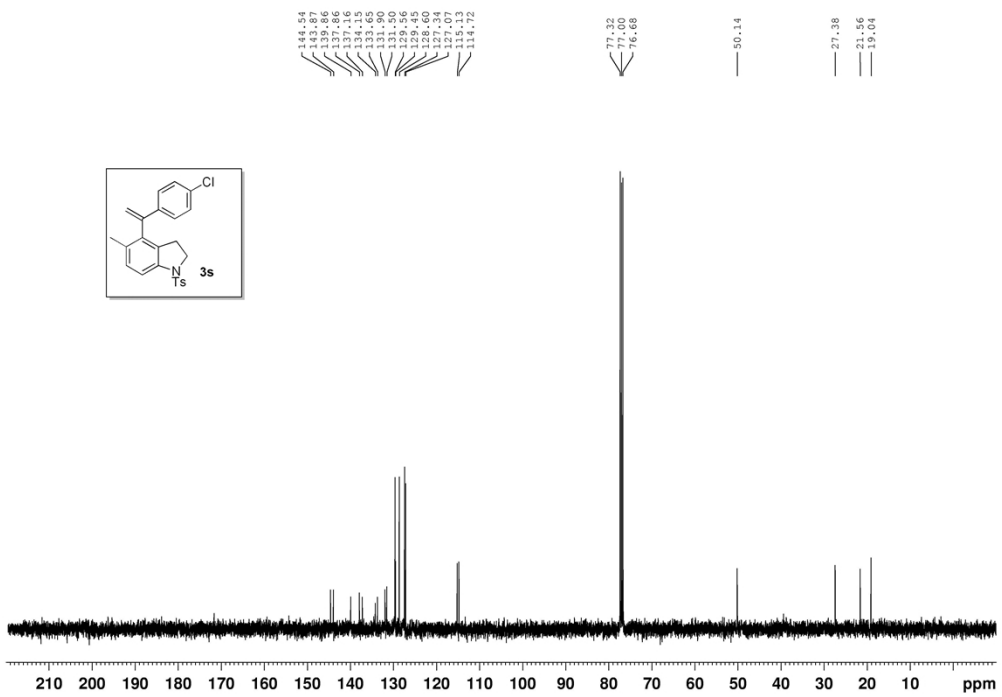
1.59
3.23
3.11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127.34
127.07
115.13
114.72
77.32
77.00
76.68
50.14
27.38
21.56
19.04
Cl
N
Ts
3s
210
200
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150
140
130
120
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80
70
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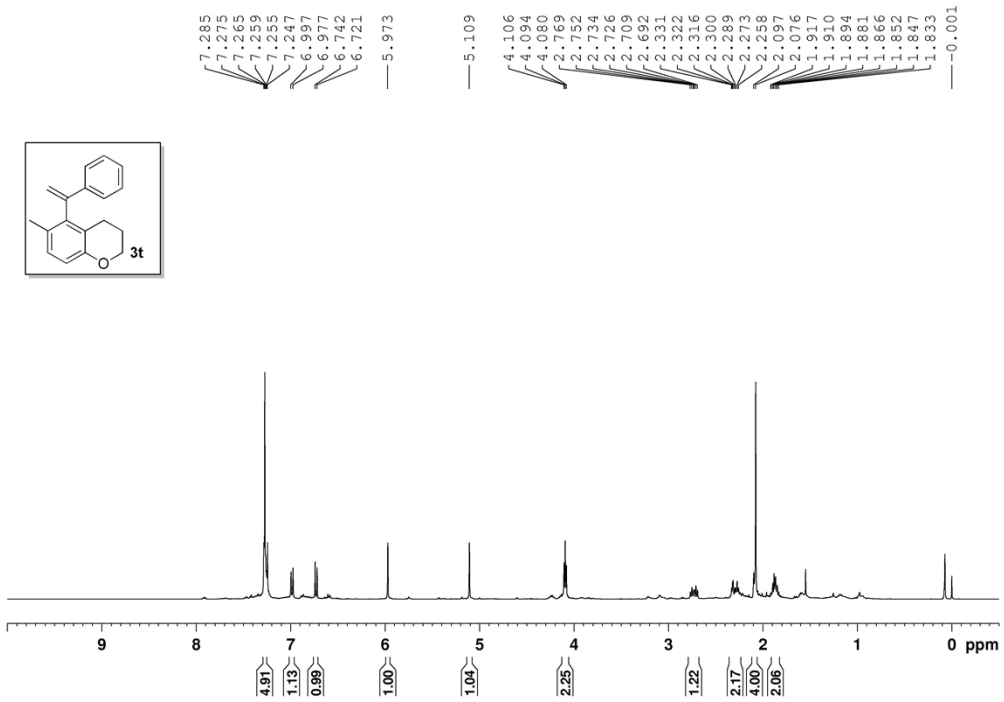
30
20
10
ppm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4.094
4.080
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2.752
2.734
2.726
2.709
2.692
2.331
2.322
2.316
2.300
2.289
2.273
2.258
2.097
2.076
1.917
1.910
1.894
1.881
1.866
1.852
1.847
1.833
0.001
3t
9
8
7
6
5
4
3
2
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1.13
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1.00
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2.25
1.22
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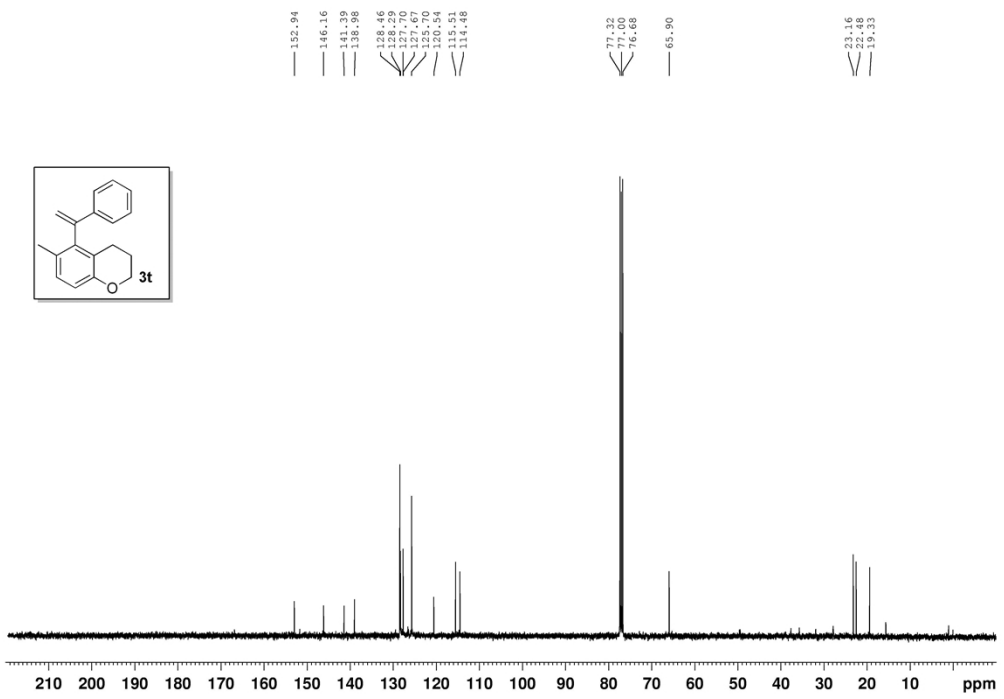
4.00
2.06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125.70
120.54
115.51
114.48
77.32
77.00
76.68
65.90
23.16
22.48
19.33
3t
210
200
190
180
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150
140
130
120
110
100
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70
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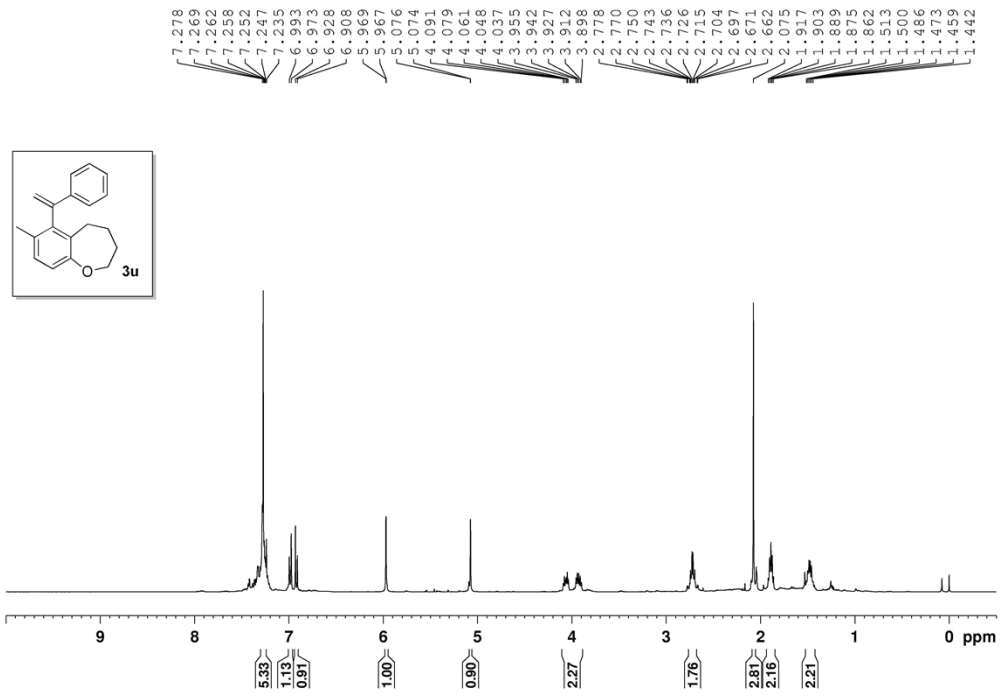
30
20
10
ppm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5.967
5.076
5.074
4.091
4.079
4.061
4.048
4.037
3.955
3.942
3.927
3.912
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2.770
2.750
2.743
2.736
2.726
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2.697
2.671
2.662
2.075
1.917
1.903
1.889
1.875
1.862
1.513
1.500
1.486
1.473
1.459
1.442
3u
9
8
7
6
5
4
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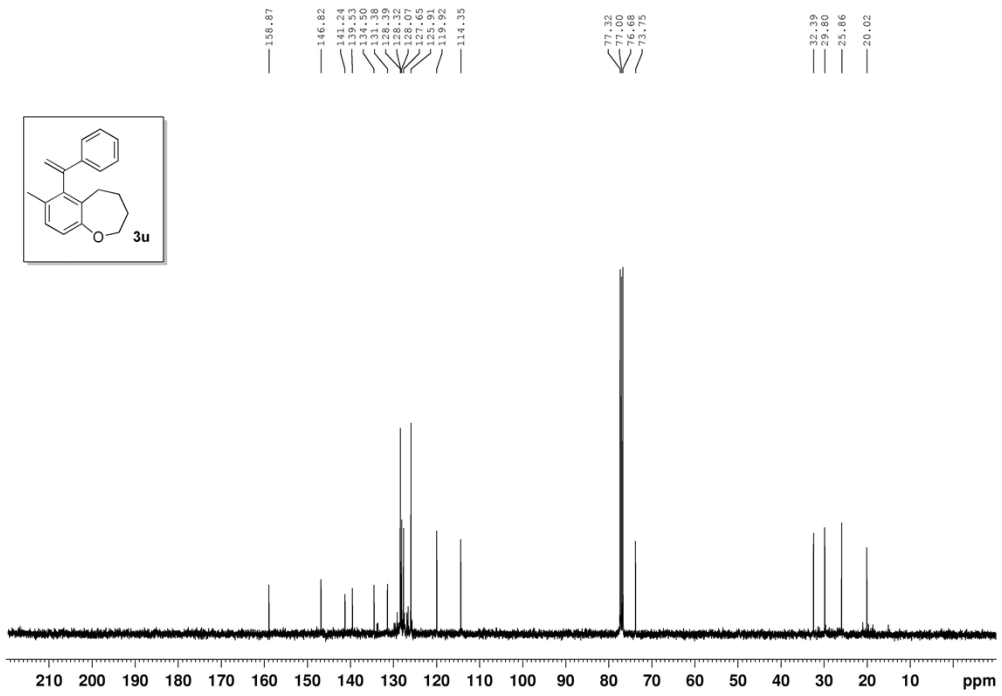
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127.65
125.91
119.92
114.35
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77.00
76.68
73.75
32.39
29.80
25.86
20.02
3u
210
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180
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150
140
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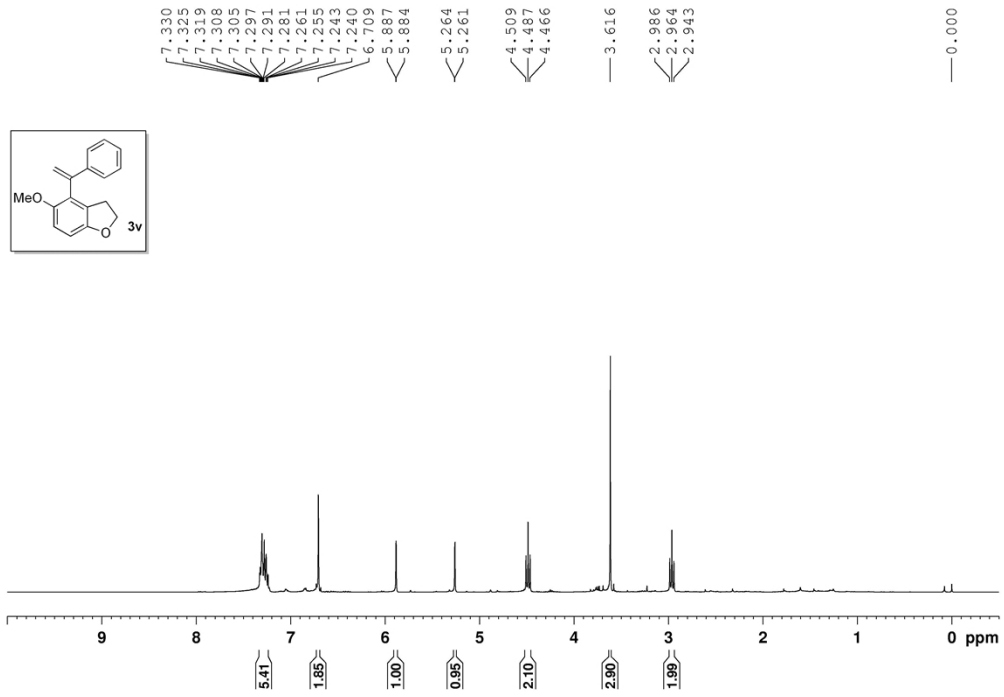
20
10
ppm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7.261
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5.887
5.884
5.264
5.261
4.509
4.487
4.466
3.616
2.986
2.964
2.943
0.000
MeO
3v
9
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3
2
1
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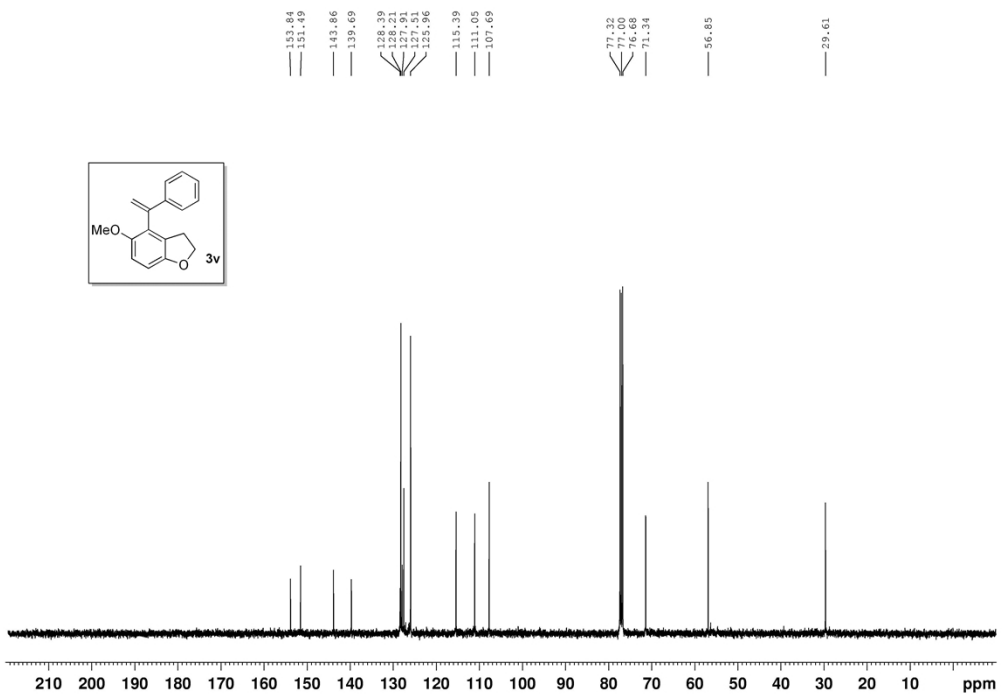
2.90
1.99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111.05
107.69
77.32
77.00
76.68
71.34
56.85
29.61
MeO
3v
210
200
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150
140
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120
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70
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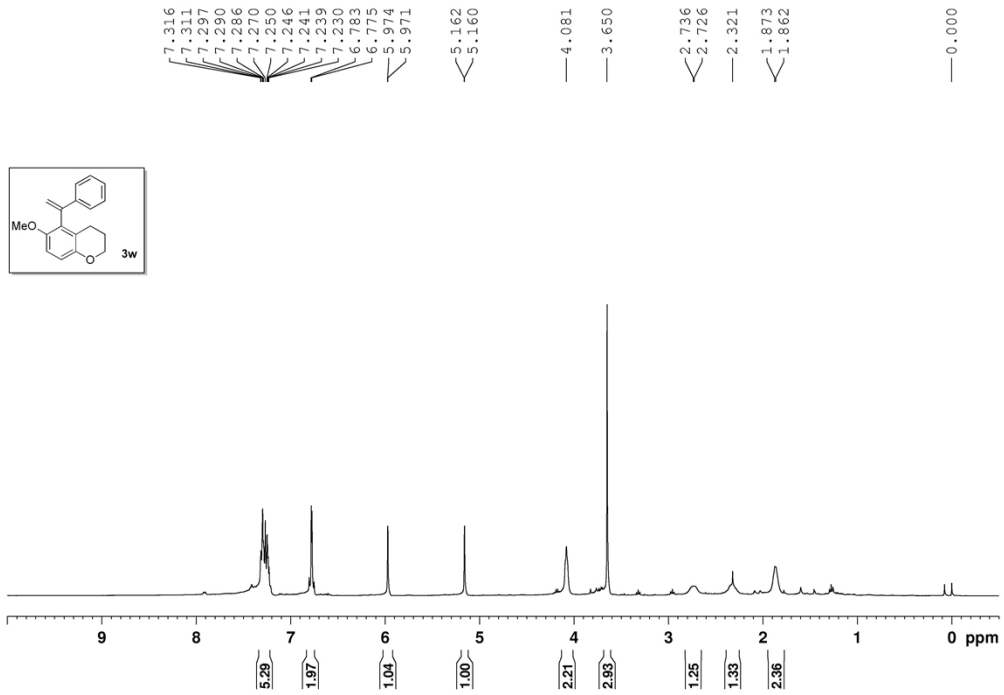
10
ppm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7.239
7.230
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5.974
5.971
5.162
5.160
4.081
3.650
2.736
2.726
2.321
1.873
1.862
0.000
MeO
3w
9
8
7
6
5
4
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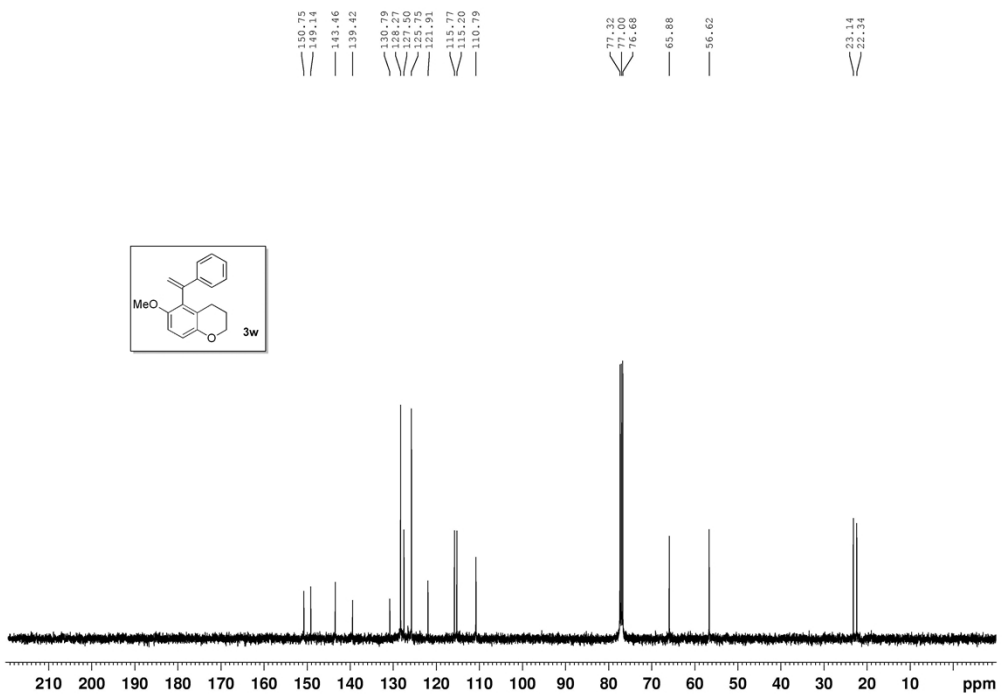
2.36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125.75
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115.77
115.20
110.79
77.32
77.00
76.68
65.88
56.62
23.14
22.34
MeO
3w
210
200
190
180
170
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150
140
130
120
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100
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70
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50
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30
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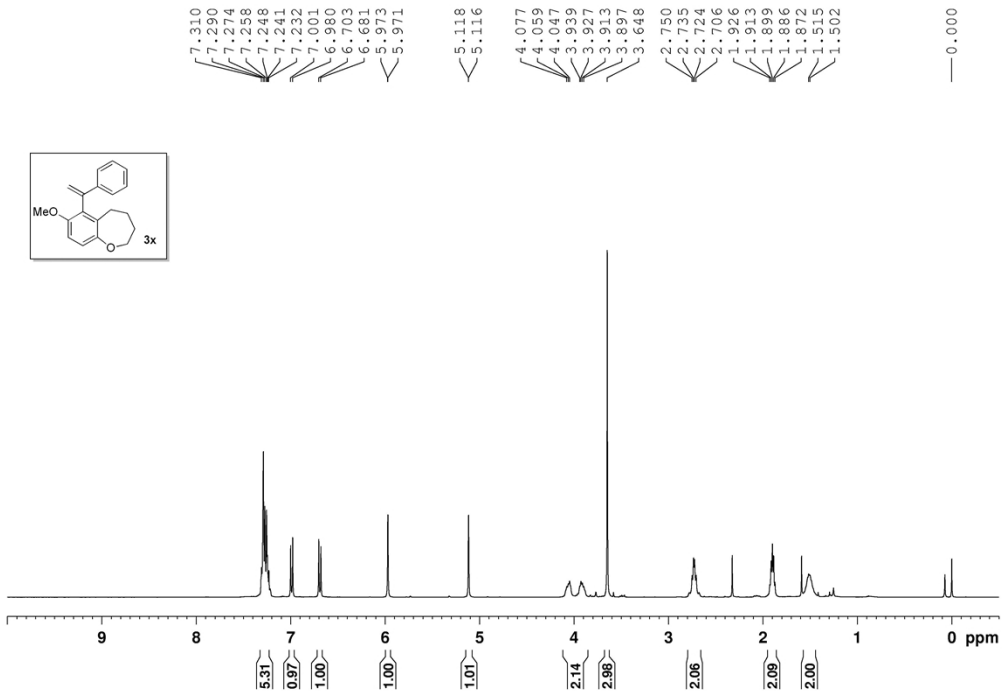
10
ppm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7.241
7.232
7.001
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6.703
6.681
5.973
5.971
5.118
5.116
4.077
4.059
4.047
3.939
3.927
3.913
3.897
3.648
2.750
2.735
2.724
2.706
1.926
1.913
1.899
1.886
1.872
1.515
1.502
0.000
MeO
3x
9
8
7
6
5
4
3
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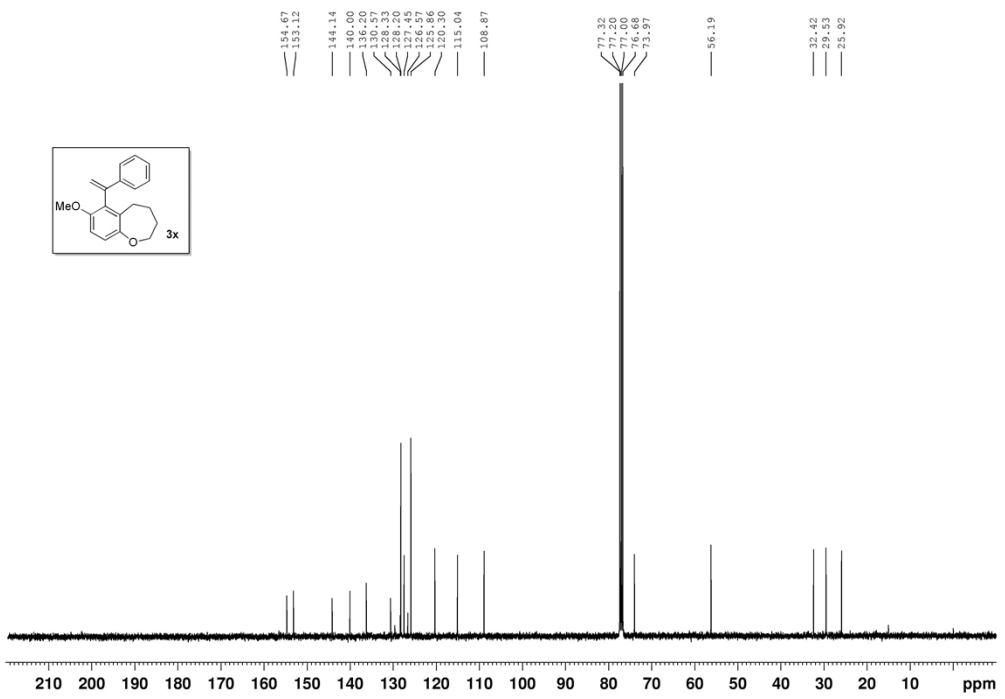
2.14
2.98
2.06
2.09
2.00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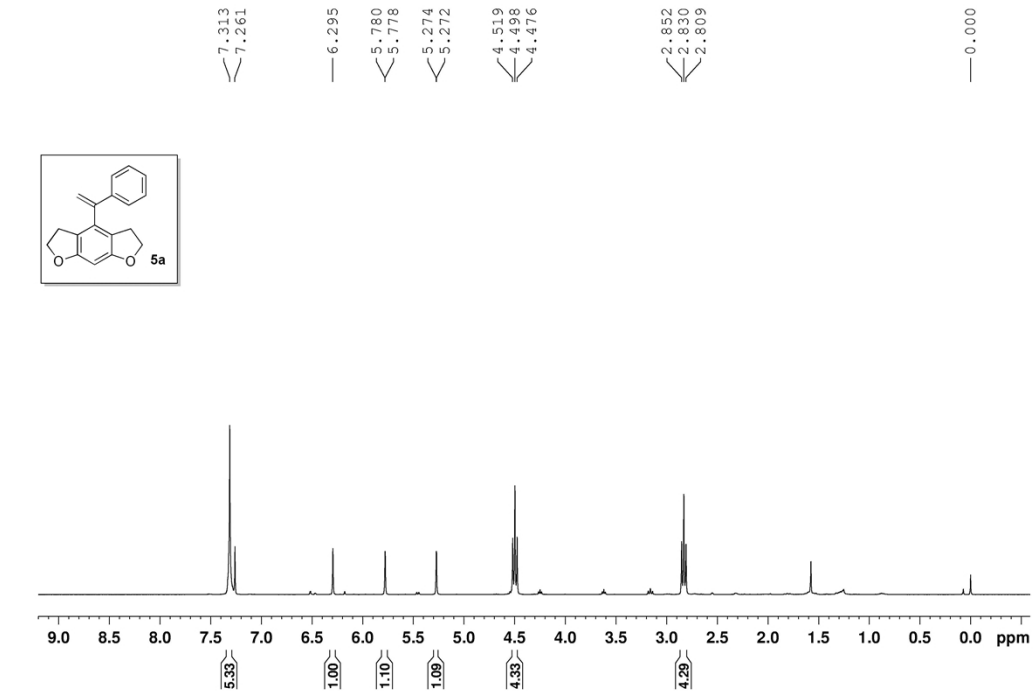
127.45
126.57
125.86
120.30
115.04
108.87
77.32
77.20
77.00
76.68
73.97
56.19
32.42
29.53
25.92
MeO
3x
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm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5.272
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4.498
4.476
2.852
2.830
2.809
0.000
5a
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm
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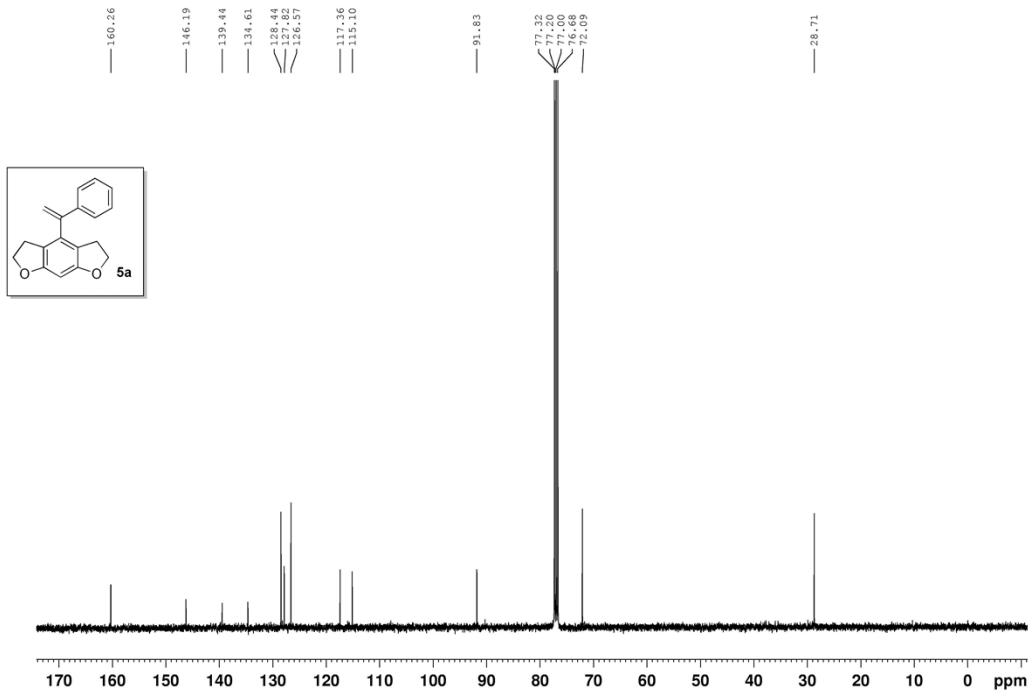
1.00
1.10
1.09
4.33
4.29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126.57
117.36
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77.20
77.00
76.68
72.09
28.71
5a
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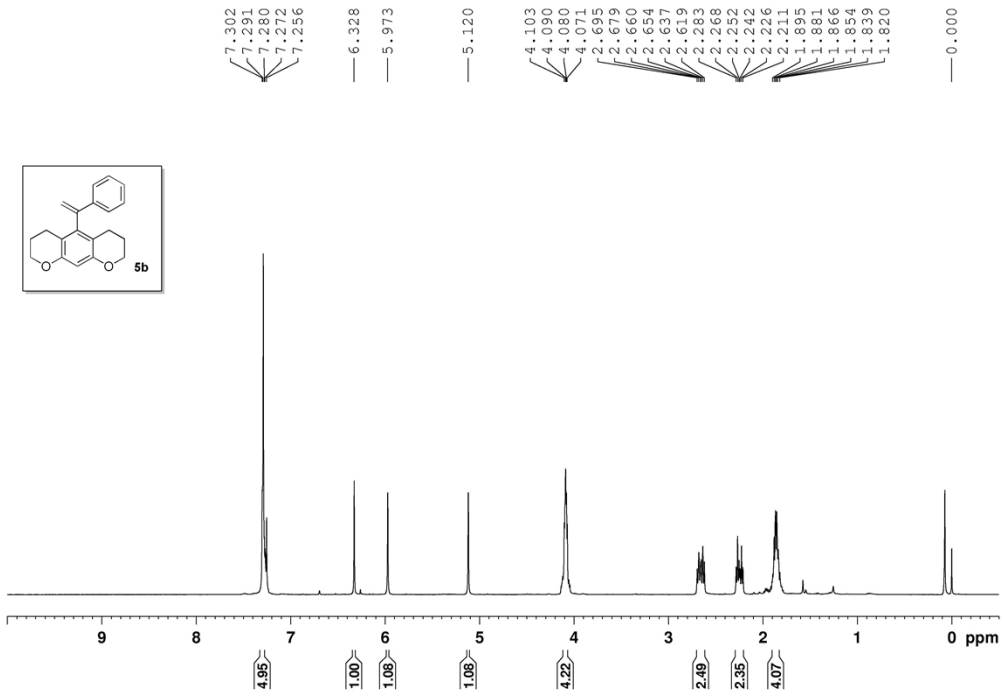
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5.120
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4.090
4.080
4.071
2.695
2.679
2.660
2.654
2.637
2.619
2.283
2.268
2.252
2.242
2.226
2.211
1.895
1.881
1.866
1.854
1.839
1.820
0.000
5b
9
8
7
6
5
4
3
2
1
0 ppm
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1.08
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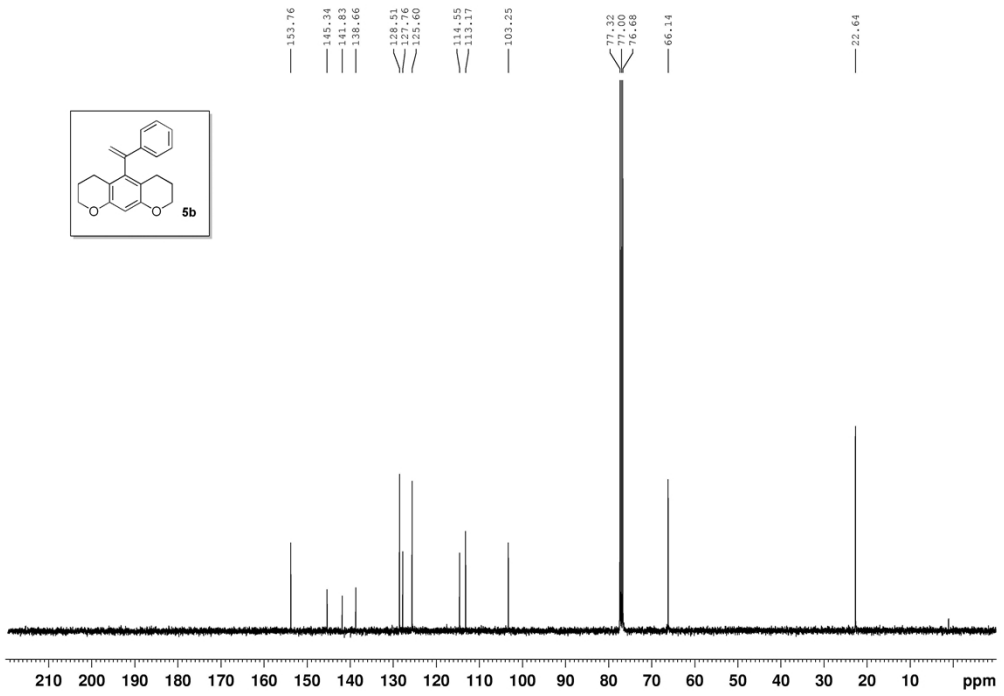
2.35
4.07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127.76
125.60
114.55
113.17
103.25
77.32
77.00
76.68
66.14
22.64
5b
210
200
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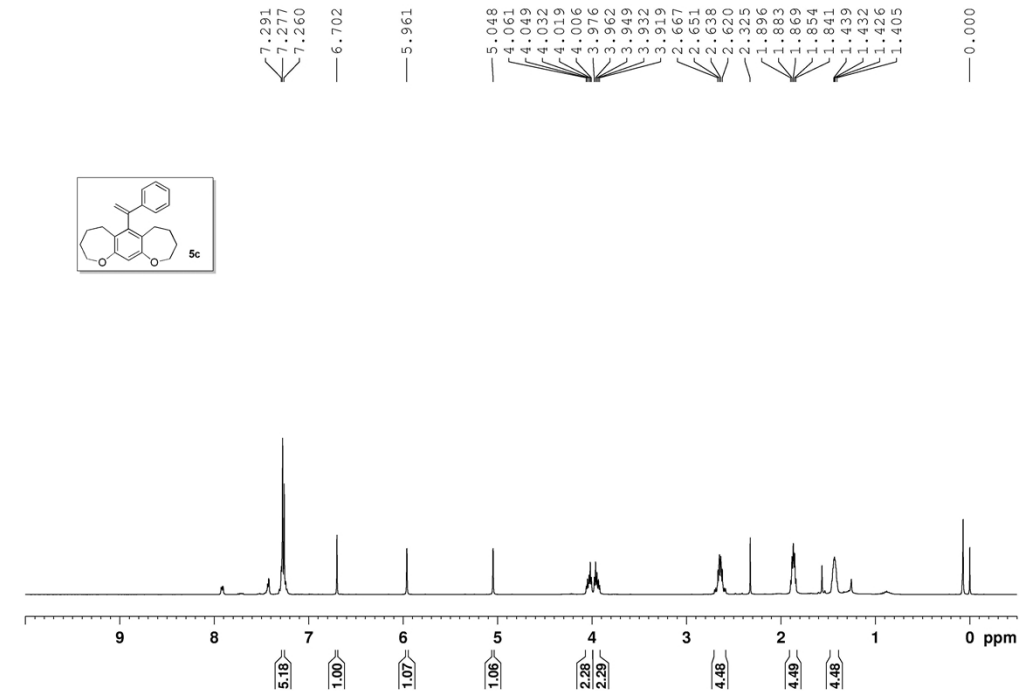
10
ppm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4.049
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4.019
4.006
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3.962
3.949
3.932
3.919
2.667
2.651
2.638
2.620
2.325
1.896
1.883
1.869
1.854
1.841
1.439
1.432
1.426
1.405
0.000
5c
9
8
7
6
5
4
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2
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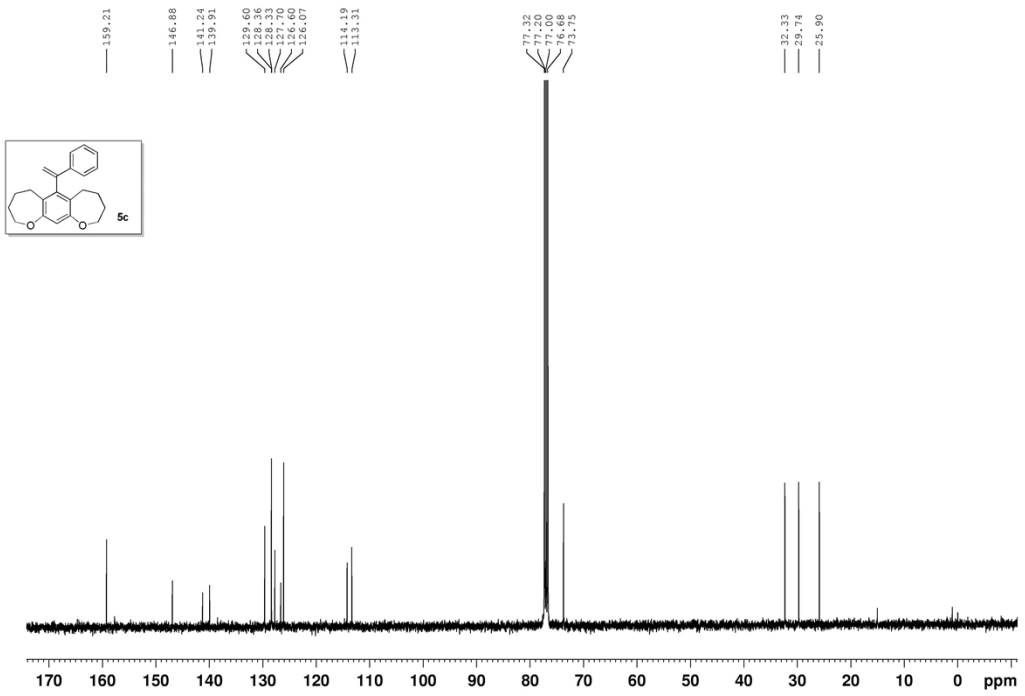
1.06
2.28
2.29
4.48
4.49
4.48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141.24
139.91
129.60
128.36
128.33
127.00
126.60
126.07
114.19
113.31
77.32
77.20
77.00
76.68
73.75
32.33
29.74
25.90
5c
170
160
150
140
130
120
110
100
90
80
70
60
50
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20
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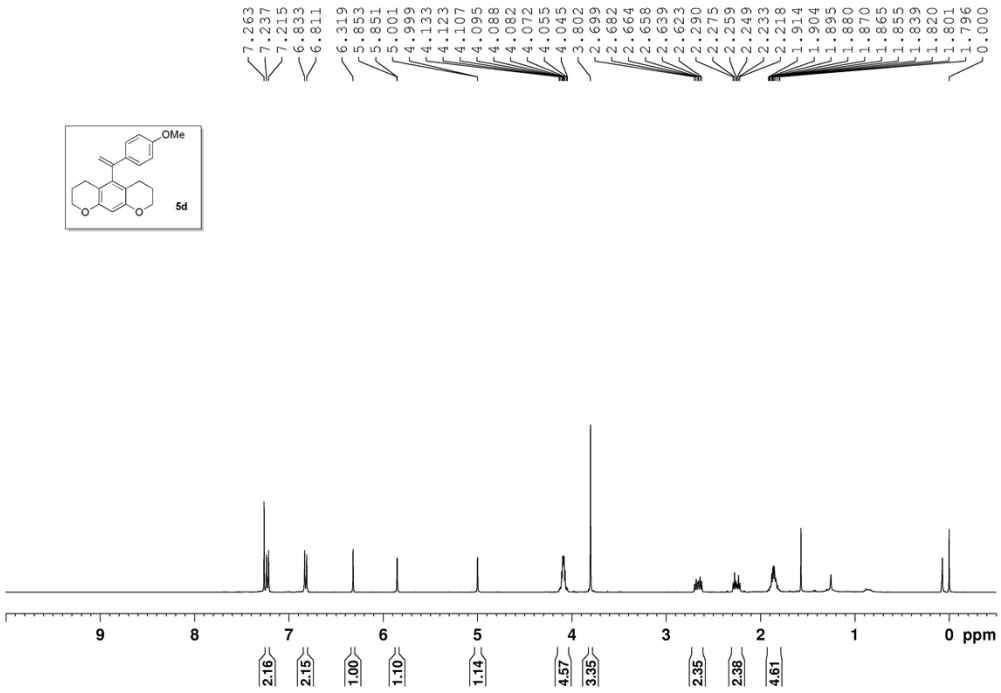
ppm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6.811
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5.851
5.001
4.999
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4.123
4.107
4.095
4.088
4.082
4.072
4.055
4.045
3.802
2.699
2.682
2.664
2.658
2.639
2.623
2.290
2.275
2.259
2.249
2.233
2.218
1.914
1.904
1.895
1.880
1.870
1.865
1.855
1.839
1.820
1.801
1.796
0.000
OMe
5d
9
8
7
6
5
4
3
2
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1.00
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1.14
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3.35
2.35
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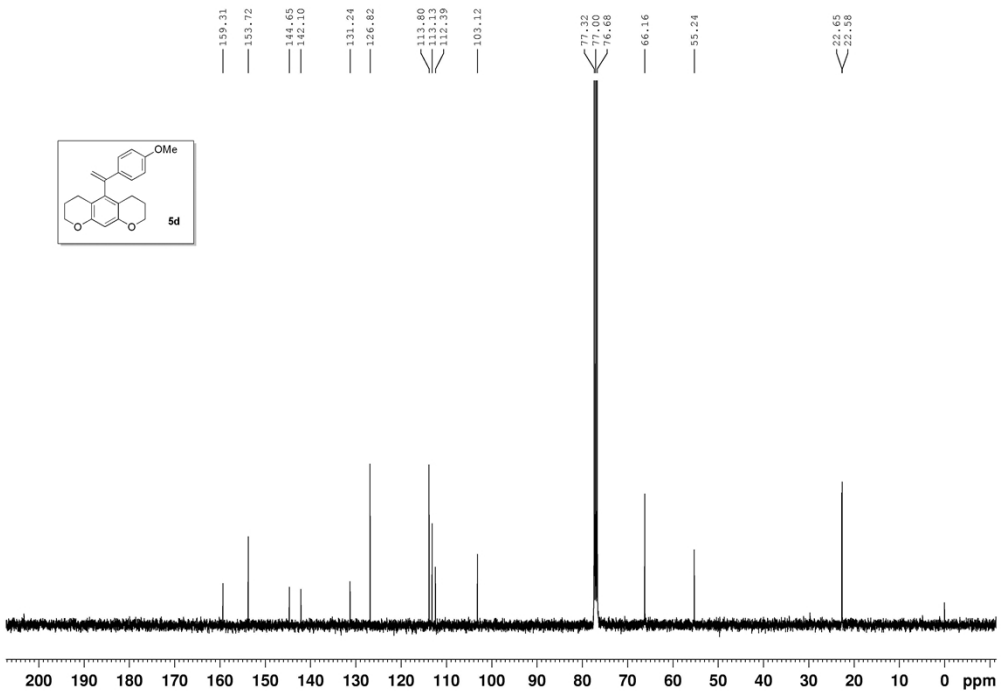
4.61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113.13
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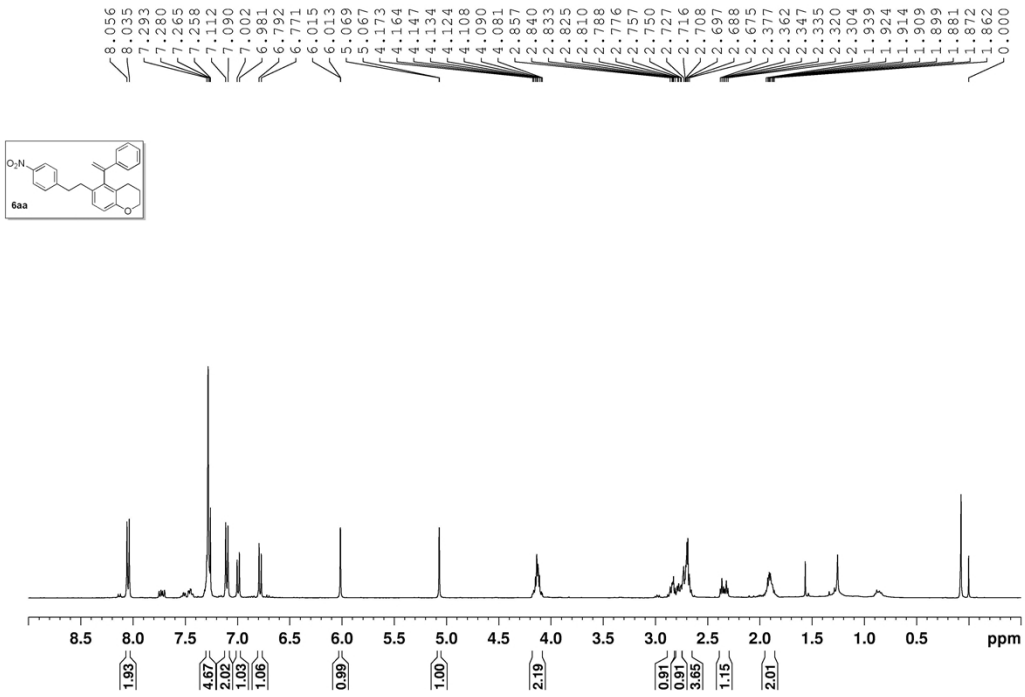
103.12
77.32
77.00
76.68
66.16
55.24
22.65
22.58
OMe
5d
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm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7.090
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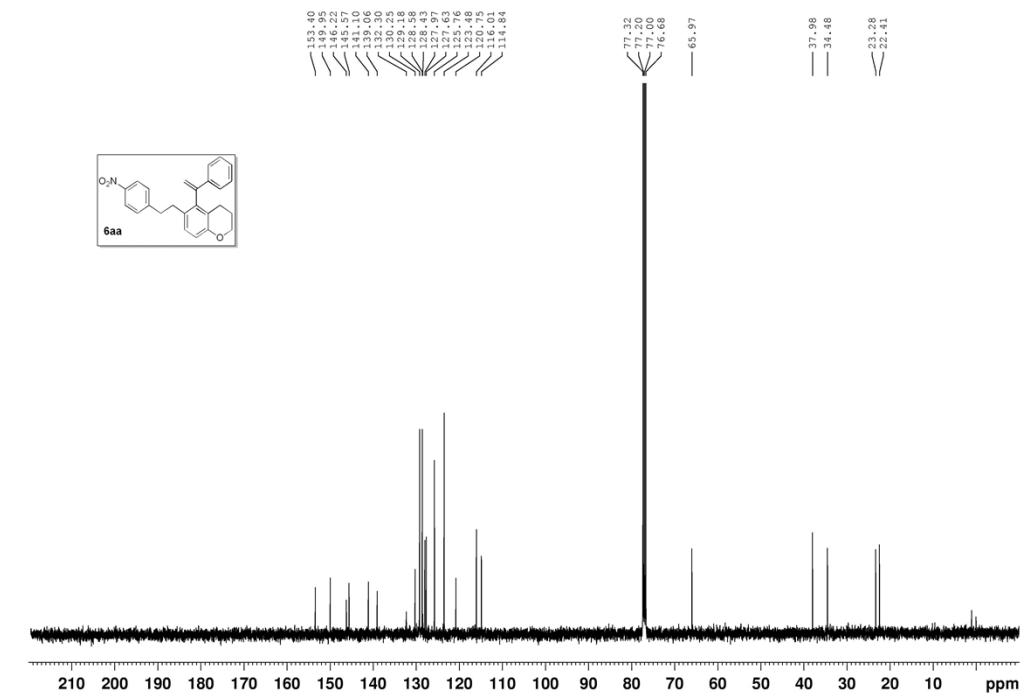
6.792
6.771
6.015
6.013
5.069
5.067
4.173
4.164
4.147
4.134
4.124
4.108
4.090
4.081
2.857
2.840
2.833
2.825
2.810
2.788
2.776
2.757
2.750
2.727
2.716
2.708
2.697
2.688
2.675
2.377
2.362
2.347
2.335
2.320
2.304
1.939
1.924
1.914
1.909
1.899
1.881
1.872
1.862
0.000
6aa
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.93 4.67 2.02 1.03 1.06 0.99 1.00 2.19 0.91 0.91 3.65 1.15 2.01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125.76
123.48
120.75
120.01
114.84
77.32
77.20
77.00
76.68
65.97
37.98
34.48
23.28
22.41
6aa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm